

Chemistry–A European Journal

Supporting Information

Multinuclear Pt^{II} Complexes: Why Three is Better Than Two to Enhance Photophysical Properties

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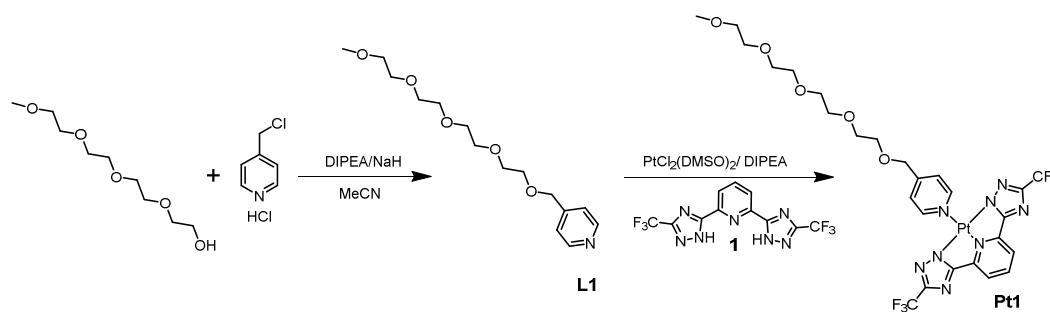
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Experimental Section.

Synthesis and Characterization. All the reactions were carried out under inert atmosphere (Schlenk technique). All the solvents were used as received from Aldrich or Fluka without any further purification. All the chemicals were purchased and used as received. The compounds were purified by column chromatography by using silica gel 60 (230–400 mesh) as stationary phase. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance 400/500 spectrometer. The ^1H NMR chemical shifts (δ) are given in ppm and referred to residual protons on the corresponding deuterated solvent. All deuterated solvents were used as received without any further purification. All coupling constants (J) are given in Hertz (Hz). Electrospray ionization mass (ESI-MS) spectra were recorded on a Bruker Daltonics (Bremen, Germany) MicroTof with loop injection.

Photophysics. *Room temperature in solution.* Absorption spectra were measured on a Shimadzu UV-3600 spectrophotometer double-beam UV–VIS–NIR spectrometer and baseline corrected. Steady-state emission spectra were recorded on a Horiba Jobin–Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation, and emission monochromators (2.1 nm mm^{−1} of dispersion; 1200 grooves mm^{−1}) and a TBX-04 single photoncounting detector. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Timeresolved measurements were performed using either the time-correlated single-photon counting (TCSPC) electronics PicoHarp300 or the Multi-Channel Scaling (MCS) electronics NanoHarp 250 of the PicoQuant FluoTime 300 (PicoQuant GmbH, Germany), equipped with a PDL 820 laser pulse driver. A pulsed laser diode LDH-P-C-375 ($\lambda = 375$ nm, pulse FWHM <70 ps, repetition rate 200 kHz – 40 MHz) was used to excite the sample and mounted directly on the sample chamber at 90°. The photons were collected by a PMA-C-192 photomultiplier (PMT) single-photon-counting detector. The data were acquired by using the commercially available software EasyTau (PicoQuant GmbH, Germany), while data analysis was performed using the commercially available software FluoFit (PicoQuant GmbH, Germany).

Synthetic procedures for mono-Pyridine Linker and mono-Platinum(II) Complex

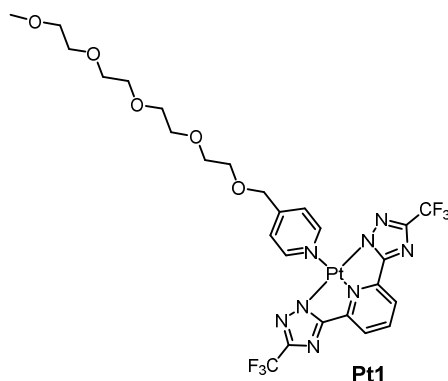


Scheme S1. Synthesis of mono-pyridine ligand **L1** and mono-Pt(II) complex **Pt1**.

Synthesis of 4-(2,5,8,11,14-pentaoxapentadecyl)pyridine (**L1**)

In a 100 mL two-neck flask under a nitrogen atmosphere, to a stirred solution of 4-chloromethyl-pyridine hydrochloride (246 mg, 1.5 mmol) in acetonitrile (20.0 mL) were Tetraethylene Glycol Monomethyl Ether (208 mg, 1 mmol) and DIPEA (355 μ L, 3 mmol). After 1 h stirring, NaH (60% in oil, 240 mg, 6 mmol) was added and the mixture was stirred overnight at 80 °C. The progress of the reaction was monitored by TLC and the reaction mixture was concentrated under vacuum. The obtained crude product was then purified over basic alumina (eluting with a gradient of DCM to DCM/MeOH, 95/5 v/v) to obtain *mono*-Pyridine linker **L1** (240 mg, 80%) as a yellowish color oil. ¹H NMR (400 MHz, CDCl₃): δ 8.59 (d, J = 6.0 Hz, 2H, Py-*H*), 7.29 (d, J = 6.3 Hz, 2H, Py-*H*), 4.61 (s, 2H, Py-CH₂-O), 4.05 – 3.62 (m, 16H, -OCH₂-), 3.39 (s, 3H, -OCH₃).; ¹³C NMR (126 MHz, CDCl₃): δ 149.6, 147.6, 121.7, 71.8, 71.3, 70.6, 70.5, 70.4, 70.1, 58.92. ESI-MS: calcd for C₁₅H₂₅NO₅+Na⁺: 323.1733 ([M+Na]⁺); found 323.1785.

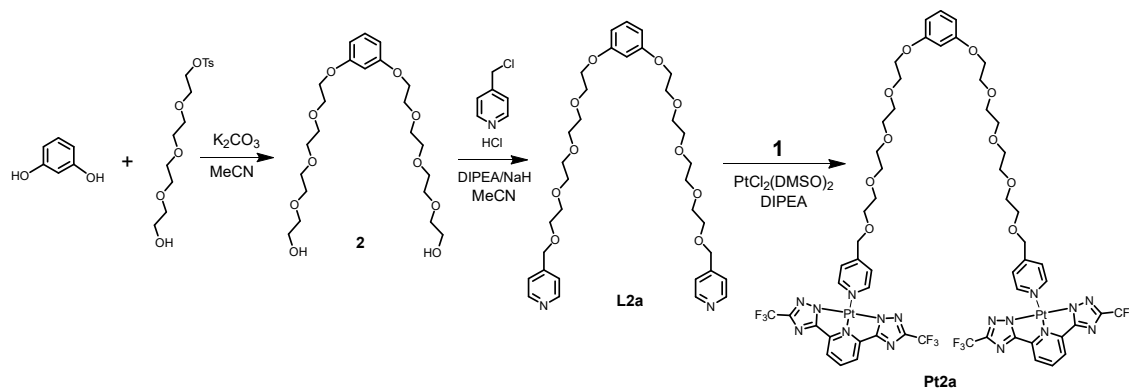
Synthesis of mono-Pt(II) complex (**Pt1**)



In a 25 mL two-neck flask equipped with a Liebig condenser under a nitrogen atmosphere, to a stirred solution of **L1** (51 mg, 0.17 mmol) in chloroform (10 mL), 2,6-bis[3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl]pyridine¹ **1** (59 mg, 0.17 mmol),

PtCl₂(DMSO)₂ (72 mg, 0.17 mmol) and Ethyl-*N,N*-diisopropylamine (70 μ L, 0.40 mmol) were added. The mixture was heated at 50 °C, and progress of the reaction was followed by ESI-MS analysis. After overnight of heating solvent evaporation of the reaction mixture afforded a crude product that was purified over neutral alumina (CH₂Cl₂/MeOH, 99.5:0.5) to obtain **Pt1** (100 mg, 70 %) as a yellow fluorescent solid. ¹H NMR (400 MHz, CDCl₃) δ 9.56 (d, *J* = 6.7 Hz, 2H, Py-*H*), 8.03 (t, *J* = 7.9 Hz, 1H, Py-*H*), 7.80 (d, *J* = 7.9 Hz, 2H, Py-*H*), 7.61 (d, *J* = 6.6 Hz, 2H, Py-*H*), 4.76 (s, 2H, Py-CH₂-), 3.80 (q, *J* = 4.8 Hz, 4H, -OCH₂-), 3.76 – 3.63 (m, 12H, -OCH₂-), 3.39 (s, 3H, -OCH₃).; ¹³C NMR (100.6 MHz, CDCl₃): δ 59.0, 70.5, 70.6, 70.6, 70.7, 70.9, 117.8, 119.5 (q, ¹*J*_{C-F} = 269 Hz), 123.5, 142.7, 147.8, 152.0, 152.2 (q, ²*J*_{C-F} = 38 Hz), 152.7, 163.1 ppm.; ¹⁹F NMR (377 MHz, CD₂Cl₂): δ -64.21. HR-MS (ESI): *m/z* calcd for C₂₆H₂₈F₆N₈O₅Pt: 842.1735 ([M]⁺) and C₂₆H₂₈F₆N₈O₅Pt+Na⁺:864.1627 ([M+Na]⁺); found 842.1794 and 864.1673.

Synthetic procedures for bis-Pyridine Linkers and bis-Platinum(II) Complexes.

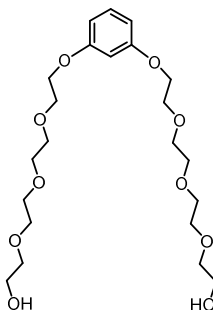


Scheme S2. Synthesis of *bis*-pyridine ligand **L2a** and *bis*-Pt(II) complex **Pt2a**.

Synthesis

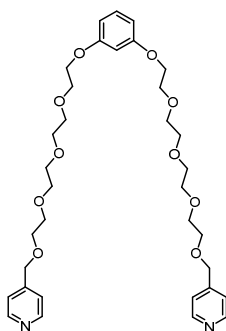
of

2,2'-((((((1,3-phenylenebis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-1-ol) (2)



2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl *p*-tosylate (835 mg, 2.4 mmol), Resorcinol (110 mg, 1 mmol), KI (50 mg, 0.3 mmol), and dry K₂CO₃ (1 g, 7.24 mmol) in dry DMF (15 mL) were stirred at 80 °C for 24 h under nitrogen atmosphere. After the complete disappearance of pyrogallol, monitored through TLC, the solvent was evaporated under vacuum, and the residue was partitioned between water (20 mL) and CH₂Cl₂ (40 mL). The aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL), and the combined organic layer was dried over anhydrous Na₂SO₄. After evaporating the solvent, the residue was purified by column chromatography (eluent: CH₂Cl₂/MeOH, 10/1, v/v) to obtain compound **2** as a colorless liquid (330 mg, 71%). ¹H NMR (400 MHz, CDCl₃): δ 7.17 (t, *J* = 8.4 Hz, 1H, Ph-*H*), 6.53 (d, *J* = 6.6 Hz, 3H, Ph-*H*), 4.13 (t, *J* = 4.8 Hz, 4H, -OCH₂-), 3.87 (t, *J* = 4.8 Hz, 4H, -OCH₂-), 3.81 – 3.67 (m, 24H, -OCH₂-); ¹³C NMR (101 MHz, CDCl₃) δ 159.89, 129.85, 107.07, 101.77, 72.49, 70.70, 70.60, 70.52, 70.26, 69.66, 67.35, 61.59. ESI-MS: calcd for C₂₂H₃₉O₁₀: 463.2543 ([M+H]⁺) and C₂₂H₃₈O₁₀+H₂O:480.2571 ([M+H₂O]⁺); found 463.2564 and 480.2591.

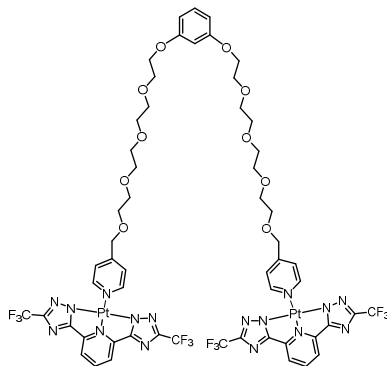
Synthesis of 1,3-bis((1-(pyridin-4-yl)-2,5,8,11-tetraoxatridecan-13-yl)oxy)benzene (L2a**)**



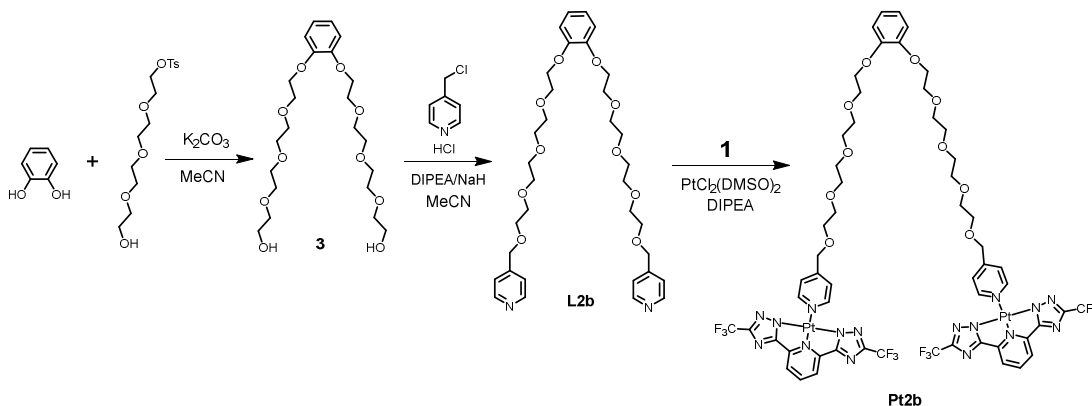
In a 100 mL two-neck flask under a nitrogen atmosphere, to a stirred solution of 4-chloromethyl-pyridine hydrochloride (164 mg, 1 mmol) in acetonitrile (20.0 mL) were added **2** (150 mg, 0.325 mmol) and DIPEA (355 μL, 3 mmol). After 1 h stirring, NaH (60% in oil, 240 mg, 6 mmol) was added and the mixture was stirred overnight at 80 °C. The progress of the reaction was monitored by TLC and the reaction mixture was concentrated under vacuum. The obtained crude product was then purified over basic alumina (eluting with a gradient of DCM to DCM/MeOH, 95/5 v/v) to obtain *bis*-Pyridine linker **L2a** (100 mg, 49%) as a yellowish color oil. ¹H NMR (500 MHz, CDCl₃) δ 8.47 (d, *J* = 5.8 Hz, 4H, Py-*H*), 7.19-7.14 (m, 5H, Py-*H*, Ph-*H*), 6.55 – 6.31 (m, 3H, Ph-*H*), 4.50 (s, 4H, Py-CH₂-), 4.00 (t, *J* = 4 Hz, 4H, -OCH₂-), 3.75 (t, *J* = 4 Hz, 4H, -OCH₂-), 3.67 – 3.52 (m, 24H, -OCH₂-); ¹³C NMR (126 MHz, CDCl₃) δ 159.9, 149.7, 147.6, 129.8, 121.7, 107.0, 101.7,

71.4, 70.7, 70.6, 70.6, 70.6, 70.5, 70.1, 69.6, 67.3. ESI-MS: calcd for $C_{34}H_{50}N_2O_{10}$:323.17 ($[M+2H]^{2+}$), and $C_{34}H_{49}N_2O_{10}$:645.34 ($[M+H]^+$); found 323.17 and 645.34.

Synthesis of bis-Pt(II) complex **Pt2a**

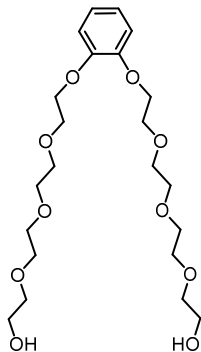


In a 25 mL two-neck flask equipped with a Liebig condenser under a nitrogen atmosphere, to a stirred solution of **L2a** (20 mg, 0.03 mmol) in chloroform (10 mL), 2,6-bis[3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl]pyridine **1** (31 mg, 0.09 mmol), $PtCl_2(DMSO)_2$ (38 mg, 0.09 mmol) and Ethyl-*N,N*-diisopropylamine (70 μ L, 0.40 mmol) were added. The mixture was heated at 50 $^{\circ}C$, and progress of the reaction was followed by ESI-MS analysis. After 2 days of heating solvent evaporation of the reaction mixture afforded a crude product that was purified over neutral alumina ($CH_2Cl_2/MeOH$, 99:1) to obtain **Pt2a** (28 mg, 65 %) as a yellow fluorescent solid. 1H NMR (400 MHz, CD_2Cl_2): δ 9.34 (d, J = 6.6 Hz, 4H), 7.95 (t, J = 7.9 Hz, 2H), 7.56 (d, J = 7.9 Hz, 4H), 7.42 (d, J = 6.3 Hz, 4H), 6.99 (t, J = 8.1 Hz, 1H), 6.45 – 6.31 (m, 3H), 4.71 (s, 4H), 3.99 (t, J = 4.8 Hz, 4H), 3.91 – 3.66 (m, 28H).; ^{19}F NMR (377 MHz, CD_2Cl_2): δ -64.45. HR-MS (ESI): calcd for $C_{56}H_{55}F_{12}N_{16}O_{10}Pt_2$:1729.3385 ($[M+H]^+$) and $C_{56}H_{54}F_{12}N_{16}O_{10}Pt_2+Na^+$:1751.3205 ($[M+Na]^+$); found 1729.3415 and 1751.3233.



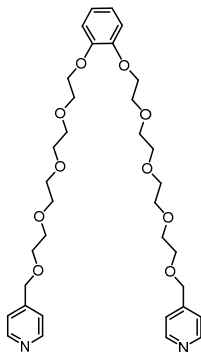
Scheme S3. Synthesis of *bis*-pyridine ligand **L2b** and *bis*-Pt(II) complex **Pt2b**.

Synthesis of 2,2'-((((((1,2-phenylenebis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(ethan-1-ol) (3)



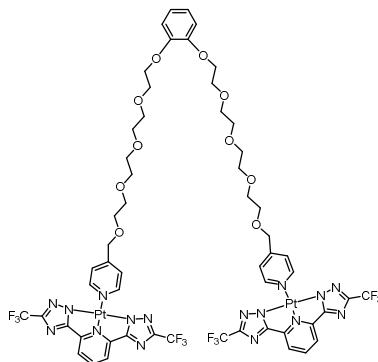
2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl *p*-tosylate (835 mg, 2.4 mmol), Resorcinol (110 mg, 1 mmol), KI (50 mg, 0.3 mmol), and dry K₂CO₃ (1 g, 7.24 mmol) in dry DMF (15 mL) were stirred at 80 °C for 24 h under nitrogen atmosphere. After the complete disappearance of pyrogallol, monitored through TLC, the solvent was evaporated under vacuum, and the residue was partitioned between water (20 mL) and CH₂Cl₂ (40 mL). The aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL), and the combined organic layer was dried over anhydrous Na₂SO₄. After evaporating the solvent, the residue was purified by column chromatography (eluent: CH₂Cl₂/MeOH, 10/1, v/v) to obtain compound **3** as a colorless liquid (350 mg, 75%). ¹H NMR (400 MHz, CDCl₃): δ 7.05 – 6.84 (m, 4H, Ph-*H*), 4.19 (t, *J* = 4.8 Hz, 4H, -OCH₂-), 3.89 (t, *J* = 4.8 Hz, 4H, -OCH₂-), 3.83 – 3.58 (m, 24H, -OCH₂-); ¹³C NMR (101 MHz, CDCl₃) δ 148.80, 121.60, 114.78, 72.52, 70.57, 70.43, 70.41, 70.14, 69.58, 68.72, 61.39. ESI-MS: calcd for C₂₂H₃₉O₁₀: 463.25 ([M+H]⁺) and C₂₂H₃₈O₁₀+H₂O:480.25 ([M+H₂O]⁺); found 463.25 and 480.25.

Synthesis of 1,2-bis((1-(pyridin-4-yl)-2,5,8,11-tetraoxatridecan-13-yl)oxy)benzene (L2b)



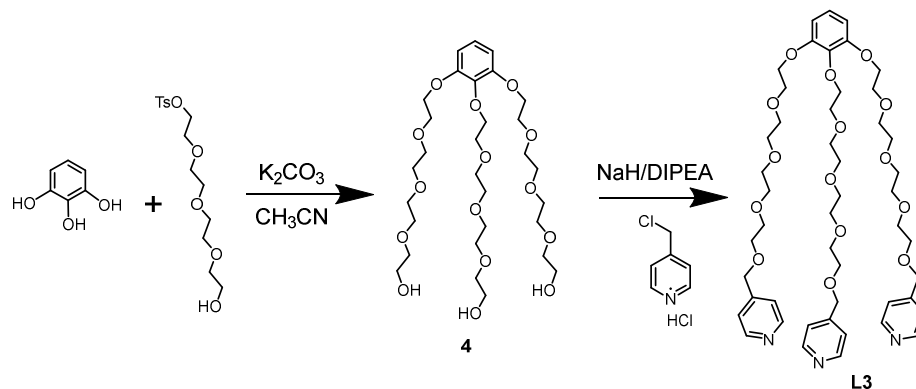
In a 100 mL two-neck flask under a nitrogen atmosphere, to a stirred solution of 4-chloromethyl-pyridine hydrochloride (164 mg, 1 mmol) in acetonitrile (20.0 mL) were added **3** (150 mg, 0.325 mmol) and DIPEA (355 μ L, 3 mmol). After 1 h stirring, NaH (60% in oil, 240 mg, 6 mmol) was added and the mixture was stirred overnight at 80 °C. The progress of the reaction was monitored by TLC and the reaction mixture was concentrated under vacuum. The obtained crude product was then purified over basic alumina (eluting with a gradient of DCM to DCM/MeOH, 95/5 v/v) to obtain *bis*-Pyridine linker **L2b** (106 mg, 51%) as a yellowish color oil. ^1H NMR (400 MHz, CDCl_3): δ 8.56 (d, J = 5.6 Hz, 4H, Py-*H*), 7.27 (d, J = 5.3 Hz, 4H, Py-*H*), 6.95 – 6.87 (m, 4H, Ph-*H*), 4.58 (s, 4H, Py- CH_2 -), 4.16 (t, J = 5.1 Hz, 4H, $-\text{OCH}_2$ -), 3.85 (t, J = 5.1 Hz, 4H, $-\text{OCH}_2$ -), 3.79 – 3.61 (m, 24H, $-\text{OCH}_2$ -); ^{13}C NMR (126 MHz, CDCl_3): δ 149.7, 148.9, 147.5, 121.8, 121.6, 114.9, 71.4, 70.7, 70.68, 70.65, 70.62, 70.5, 70.1, 69.7, 68.7. calcd for $\text{C}_{34}\text{H}_{50}\text{N}_2\text{O}_{10}$: 323.17 ($[\text{M}+2\text{H}]^{2+}$), and $\text{C}_{34}\text{H}_{49}\text{N}_2\text{O}_{10}$: 645.34 ($[\text{M}+\text{H}]^+$); found 323.17 and 645.34.

Synthesis of *bis*-Pt(II) complex **Pt2b**



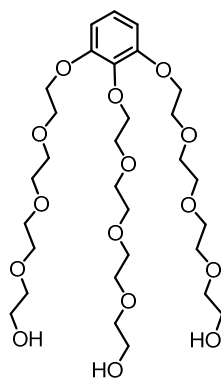
In a 25 mL two-neck flask equipped with a Liebig condenser under a nitrogen atmosphere, to a stirred solution of **L2b** (20 mg, 0.03 mmol) in chloroform (10 mL), 2,6-bis[3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl]pyridine **1** (31 mg, 0.09 mmol), $\text{PtCl}_2(\text{DMSO})_2$ (38 mg, 0.09 mmol) and Ethyl-*N,N*-diisopropylamine (70 μ L, 0.40 mmol) were added. The mixture was heated at 50 °C, and progress of the reaction was followed by ESI-MS analysis. After 2 days of heating solvent evaporation of the reaction mixture afforded a crude product that was purified over neutral alumina ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 99:1) to obtain **Pt2b** (31 mg, 60 %) as a yellow fluorescent solid. ^1H NMR (400 MHz, CD_2Cl_2): δ 9.15 (d, J = 6.5 Hz, 4H, Py-*H*), 7.84 (t, J = 7.9 Hz, 2H, Py-*H*), 7.40 (d, J = 7.9 Hz, 4H, Py-*H*), 7.29 (d, J = 6.2 Hz, 4H, Py-*H*), 7.02 – 6.67 (m, 4H, Ph-*H*), 4.68 (s, 4H, Py- CH_2 -), 4.13 (d, J = 4.8 Hz, 4H, $-\text{OCH}_2$ -), 3.92 – 3.50 (m, 28H, $-\text{OCH}_2$ -); ^{19}F NMR (377 MHz, CD_2Cl_2): δ -64.47. HR-MS (ESI): calcd for $\text{C}_{56}\text{H}_{55}\text{F}_{12}\text{N}_{16}\text{O}_{10}\text{Pt}_2$: 1729.3385 ($[\text{M}+\text{H}]^+$) and $\text{C}_{56}\text{H}_{54}\text{F}_{12}\text{N}_{16}\text{O}_{10}\text{Pt}_2+\text{Na}^+$: 1751.3205 ($[\text{M}+\text{Na}]^+$); found 1729.3465 and 1751.3286.

Synthetic procedures for tris-Pyridine Linker



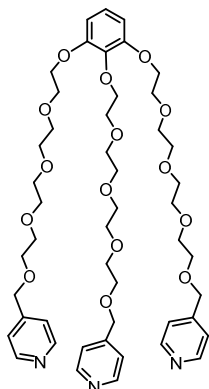
Scheme S4. Synthesis of *tris*-pyridine ligand **L3**.

Synthesis of 2,2',2''-((((((benzene-1,2,3-triyltris(oxy))tris(ethane-2,1-diyl))tris(oxy))tris(ethane-2,1-diyl))tris(oxy))tris(ethane-2,1-diyl))tris(oxy))tris(ethane-2,1-diyl))tris(oxy))tris(ethanol) (4)



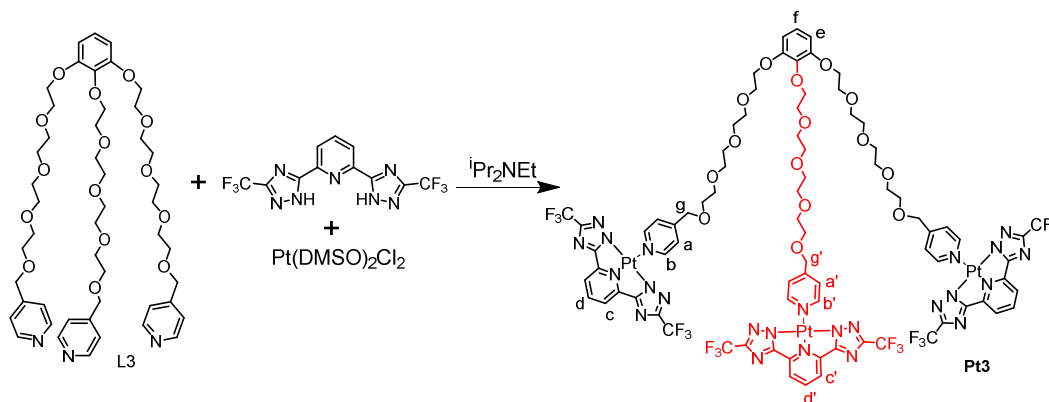
2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl *p*-tosylate (1 g, 2.87 mmol), pyrogallol (90 mg, 0.72 mmol), KI (50 mg, 0.3 mmol), and dry K_2CO_3 (1 g, 7.24 mmol) in dry DMF (15 mL) were stirred at 80 °C for 24 h under nitrogen atmosphere. After the complete disappearance of pyrogallol, monitored through TLC, the solvent was evaporated under vacuum, and the residue was partitioned between water (20 mL) and CH_2Cl_2 (40 mL). The aqueous layer was extracted with CH_2Cl_2 (3 \times 30 mL), and the combined organic layer was dried over anhydrous Na_2SO_4 . After evaporating the solvent, the residue was purified by column chromatography (eluent: CH_2Cl_2 /MeOH, 12/1, v/v) to obtain compound **4** as a colorless liquid (425 mg, 65%). 1H NMR (400 MHz, $CDCl_3$): δ 6.94 (t, J = 8.3 Hz, 1H, Ph-*H*), 6.61 (d, J = 8.4 Hz, 2H, Ph-*H*), 4.21 – 4.15 (m, 6H, $-OCH_2-$), 3.90 – 3.81 (m, 6H, $-OCH_2-$), 3.79 – 3.66 (m, 30H, $-OCH_2-$), 3.65 – 3.58 (m, 6H, $-OCH_2-$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.78, 138.36, 123.58, 107.71, 72.70, 72.61, 72.32, 70.73, 70.59, 70.52, 70.38, 70.27, 70.25, 69.71, 68.74, 61.58, 61.57. ESI-MS: calcd for $C_{30}H_{55}O_{15}$: 655.35 ($[M+H]^+$); $C_{30}H_{54}O_{15}+H_2O$: 672.35 ($[M+H_2O]^+$); found 655.35 and 672.35.

Synthesis of 4,4',4''-((benzene-1,2,3-triyltris(oxy))tris(2,5,8,11-tetraoxatridecane-13,1-diyl))tripyridine (L3)



In a 100 mL two-neck flask under a nitrogen atmosphere, to a stirred solution of 4-chloromethyl-pyridine hydrochloride (246 mg, 1.5 mmol) in acetonitrile (20.0 mL) were added **3** (200 mg, 0.3 mmol) and DIPEA (550 μ L, 3 mmol). After 1 h stirring, NaH (60% in oil, 240 mg, 6 mmol) was added and the mixture was stirred overnight at 80 $^{\circ}$ C. The progress of the reaction was monitored by TLC and the reaction mixture was concentrated under vacuum. The obtained crude product was then purified over basic alumina (eluting with a gradient of DCM to DCM/MeOH, 95:5) to obtain *tris*-Pyridine linker **L3** (222 mg, 80%) as a reddish color oil. ^1H NMR (400 MHz, MeOD): δ 8.48 (d, J = 5.9 Hz, 6H, Py-*H*), 7.43 (d, J = 5.6 Hz, 6H, Py-*H*), 6.95 (t, J = 8.3 Hz, 1H, Ph-*H*), 6.65 (d, J = 8.4 Hz, 2H, Ph-*H*), 4.62 (s, 6H, Py- CH_2 -), 4.20 – 4.08 (m, 6H, $-\text{OCH}_2$ -), 3.99 – 3.76 (m, 6H, $-\text{OCH}_2$ -), 3.76 – 3.58 (m, 36H, $-\text{OCH}_2$ -); ^{13}C NMR (100 MHz, CDCl_3): δ 152.82, 149.69, 147.63, 138.58, 123.50, 121.78, 107.93, 72.25, 71.45, 70.77, 70.66, 70.65, 70.62, 70.58, 70.56, 70.53, 70.46, 70.19, 69.73, 68.76. ESI-MS: calcd for $\text{C}_{48}\text{H}_{70}\text{N}_3\text{O}_{15}$: 928.48 ($[\text{M}+\text{H}]^+$), $\text{C}_{48}\text{H}_{71}\text{N}_3\text{O}_{15}$: 464.75 ($[\text{M}+2\text{H}]^{2+}$); found 928.48 and 464.75.

Synthesis of *tris*-Platinum(II) Complex



Scheme S5. Synthesis of *tris*-Pt(II) complex **Pt3**.

In a 25 mL two-neck flask equipped with a Liebig condenser under a nitrogen atmosphere, to a stirred solution of **L3** (28 mg, 0.03 mmol) in chloroform (7.4 mL), 2,6-bis[3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl]pyridine **1** (31 mg, 0.09 mmol), PtCl₂(DMSO)₂ (38 mg, 0.09 mmol) and Ethyl-*N,N*-diisopropylamine (70 μ L, 0.40 mmol) were added. The mixture was heated at 50 °C, and progress of the reaction was followed by ESI-MS analysis. After 4 days of heating solvent evaporation of the reaction mixture afforded a crude product that was purified by CombiFlash (CH₂Cl₂/MeOH, 9:1) to obtain **Pt3** (50 mg, 65 %) as a yellow fluorescent crystalline solid. ¹H NMR (400 MHz, CD₂Cl₂): δ 9.03 (d, *J* = 6.6 Hz, 4H, *H^b*), 8.96 (d, *J* = 6.5 Hz, 2H, *H^{b'}*), 7.76 (td, *J* = 7.9, 2.0 Hz, 3H, *H^{d,d'}*), 7.29 (d, *J* = 7.9 Hz, 4H, *H^c*), 7.25 (d, *J* = 7.8 Hz, 2H, *H^{c'}*), 7.21 (d, *J* = 6.4 Hz, 4H, *H^a*), 7.14 (d, *J* = 6.4 Hz, 2H, *H^{a'}*), 6.91 (t, *J* = 8.3 Hz, 1H, *H^f*), 6.57 (d, *J* = 8.4 Hz, 2H, *H^e*), 4.66 (s, 2H, br, *H^{g,g'}*), 4.19 – 4.12 (m, 6H), 3.94 – 3.51 (m, 42H); ¹⁹F NMR (377 MHz, CD₂Cl₂) δ : -64.092, -64.097. ESI-MS: calcd for C₈₁H₇₉F₁₈N₂₄O₁₅Pt₃+Na⁺: 2577.4705 ([M+Na]⁺); found 2577.4714.

Chemical structure: Oc1ccc(OCCCCCc2ccncc2)cc1

¹H NMR spectrum (ppm):

- 8.596, 8.581
- 7.299, 7.263
- 4.612
- 3.747, 3.725, 3.732, 3.728, 3.722, 3.711, 3.706, 3.697, 3.688, 3.686, 3.675, 3.663, 3.658, 3.651, 3.595
- 1.5

¹³C NMR spectrum (CDCl₃) of compound 10. The spectrum shows peaks at the following chemical shifts (ppm): 149.597, 147.664, 121.787, 71.837, 71.384, 70.601, 70.514, 70.402, 70.137, and 58.924. The x-axis is labeled f1 (ppm) and ranges from 170 to 20.

S12

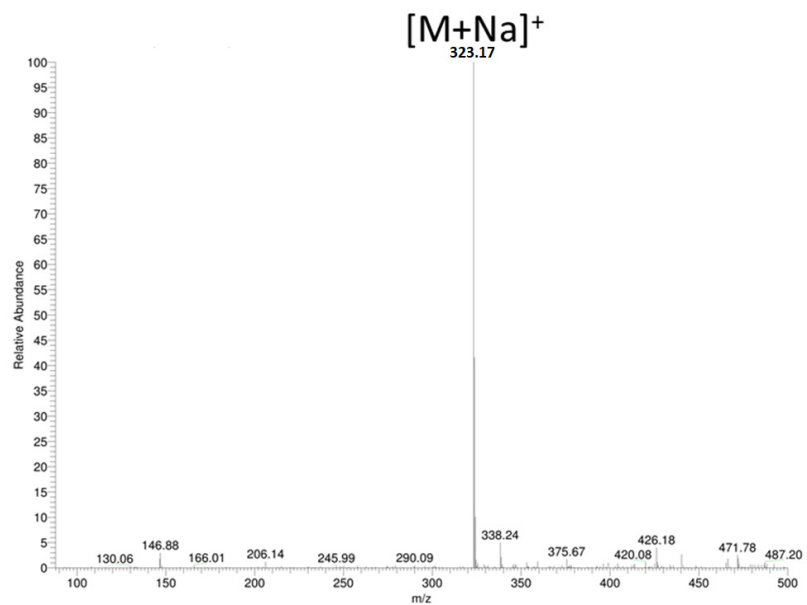


Figure S3. ESI-MS spectrum of Linker **L1**.

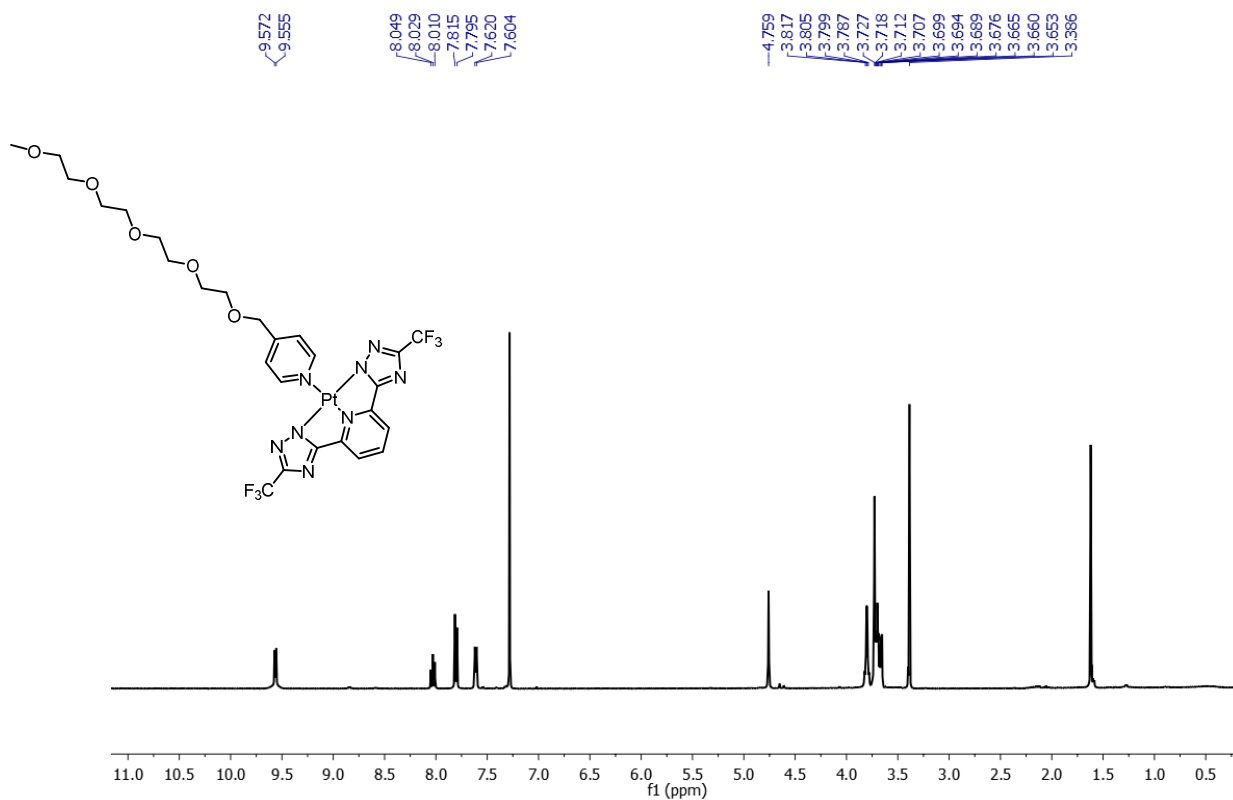


Figure S4. ¹H NMR spectrum (400 MHz) of Complex **Pt1** in CDCl₃.

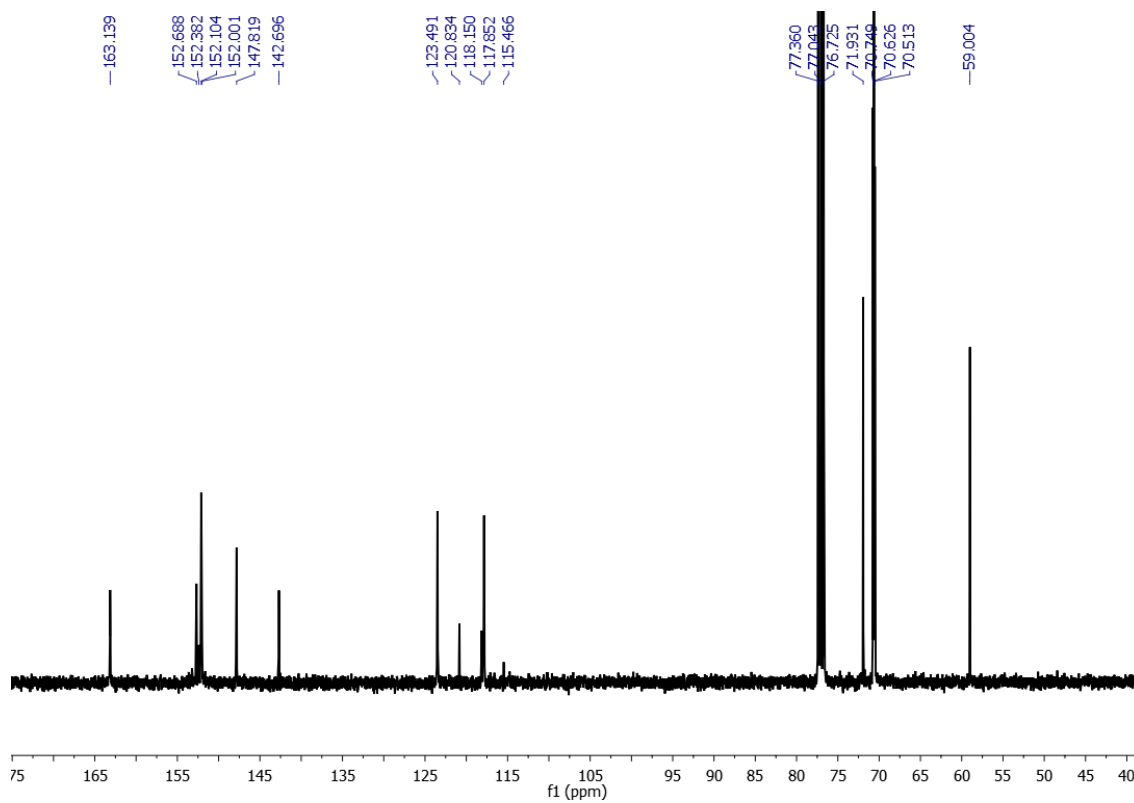


Figure S5. ¹³C NMR spectrum (100 MHz) of Complex **Pt1** in CDCl₃.

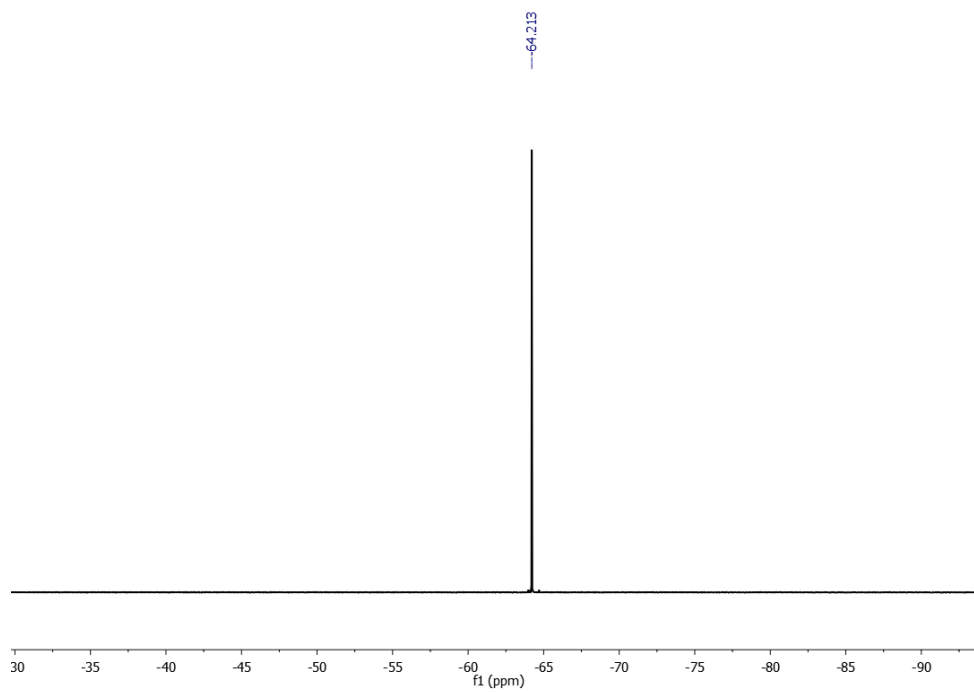


Figure S6. ¹⁹F NMR spectrum (377 MHz) of Complex **Pt1** in CDCl₃.

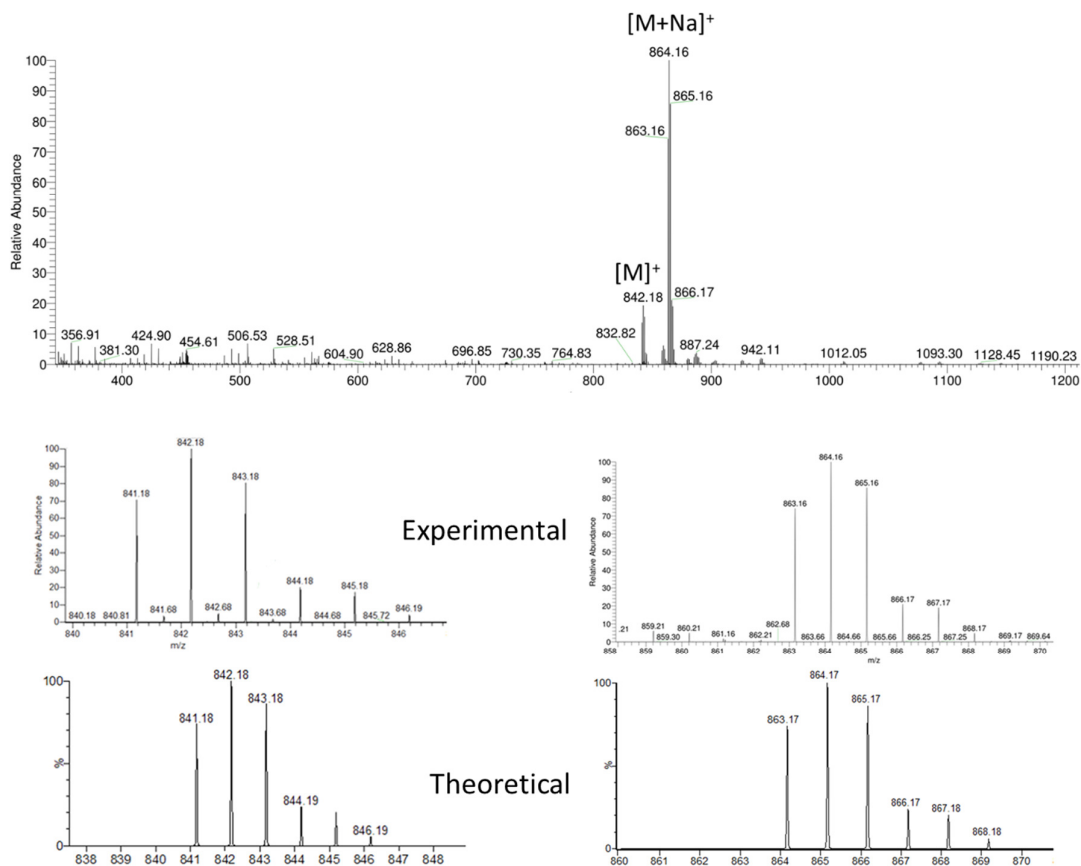


Figure S7. ESI-MS spectrum of Complex **Pt1** and Isotopic distribution of peaks.

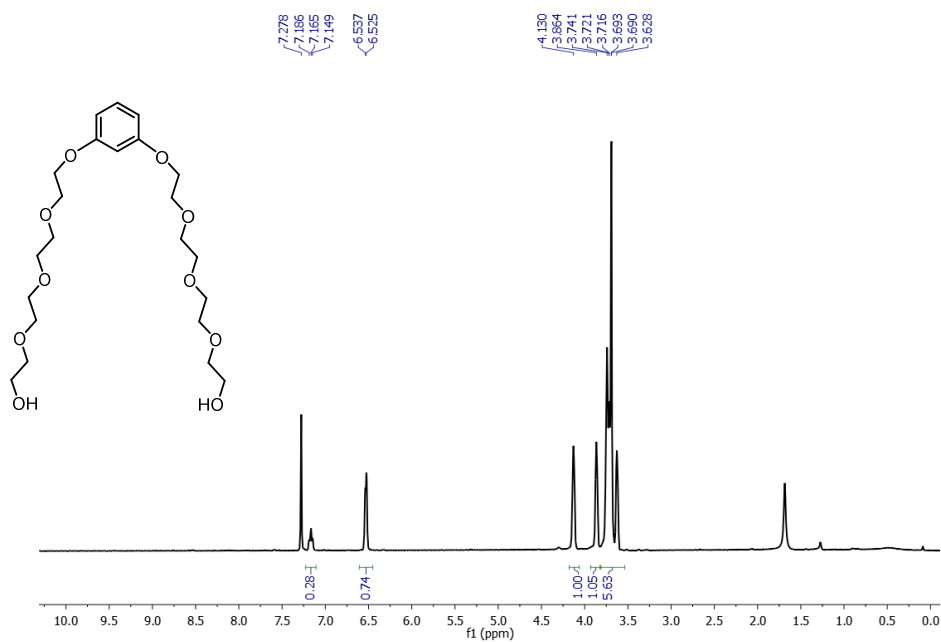


Figure S8. ^1H NMR spectrum (400 MHz) of **2** in CDCl_3 .

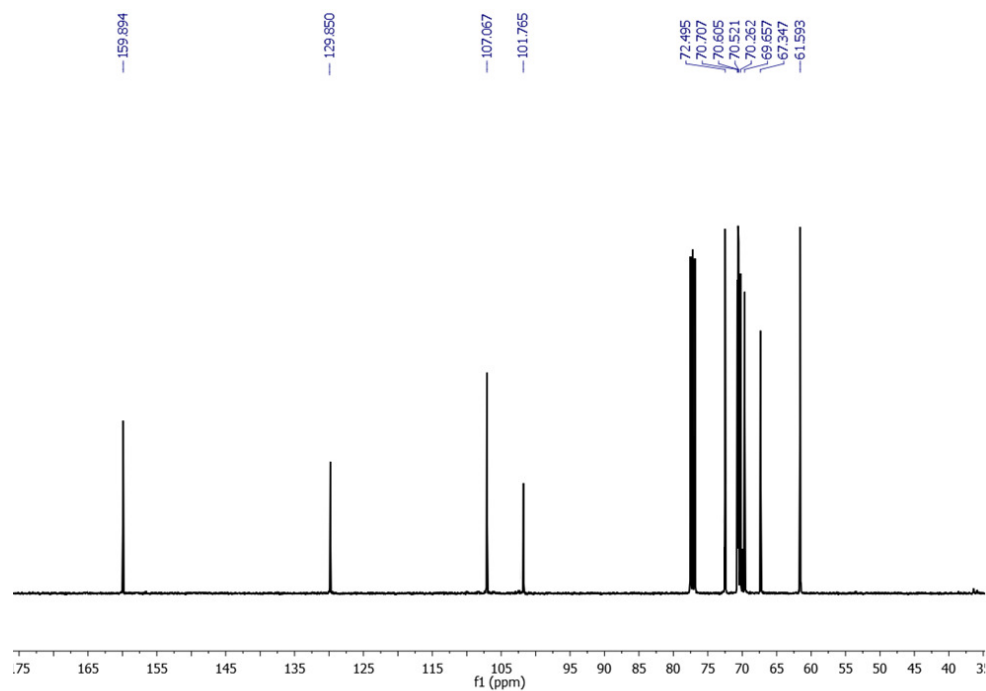


Figure S9. ^{13}C NMR spectrum (100 MHz) of **2** in CDCl_3 .

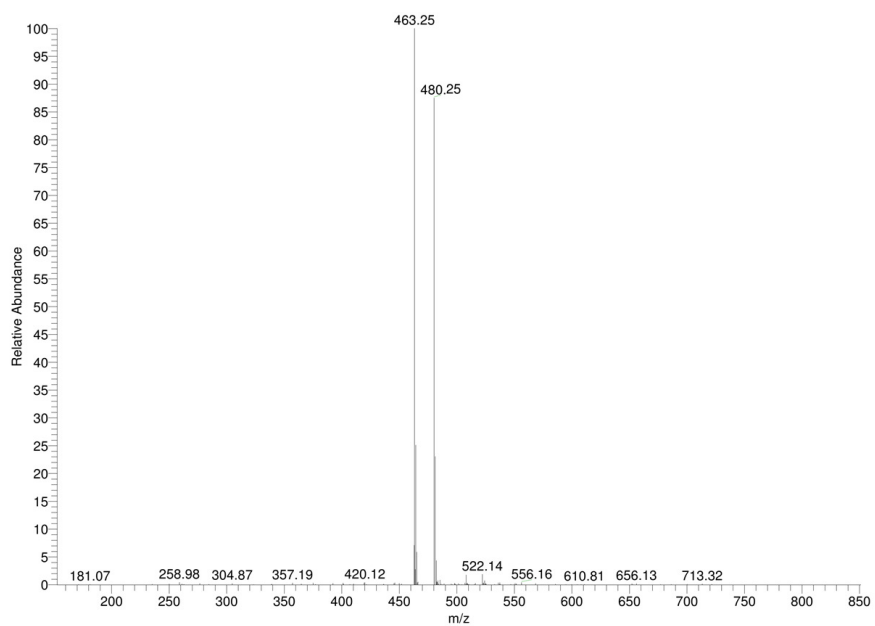
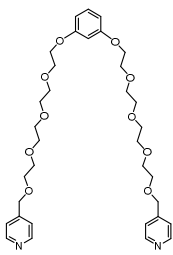


Figure S10. ESI-MS spectrum of **2**.



-159.907
 -149.718
 -147.598
 -139.795
 -121.789
 -107.017
 -101.737
 71.449
 70.776
 70.661
 70.623
 70.603
 70.558
 70.178
 69.668
 67.352



S17

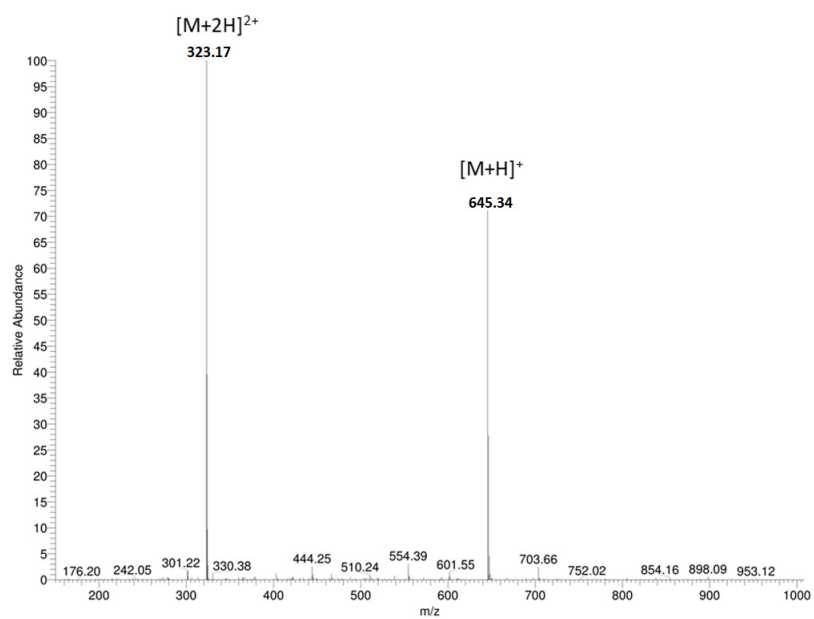


Figure S13. ESI-MS spectrum of linker **L2a**.

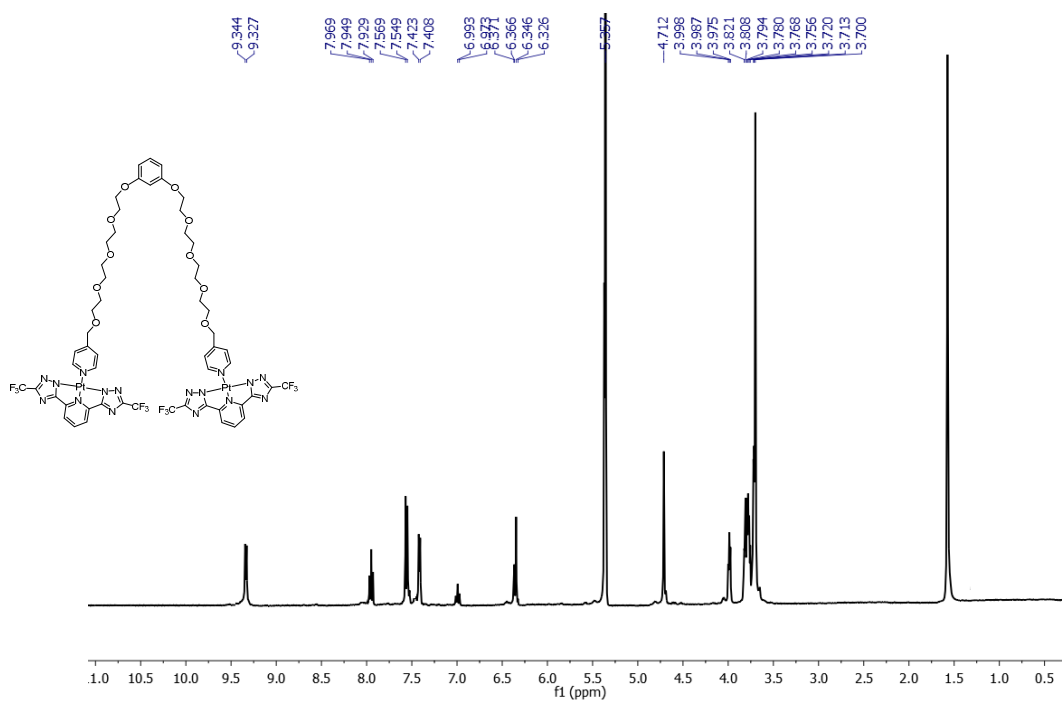


Figure S14. ^1H NMR spectrum (400 MHz) of complex **Pt2a** in CD_2Cl_2 .

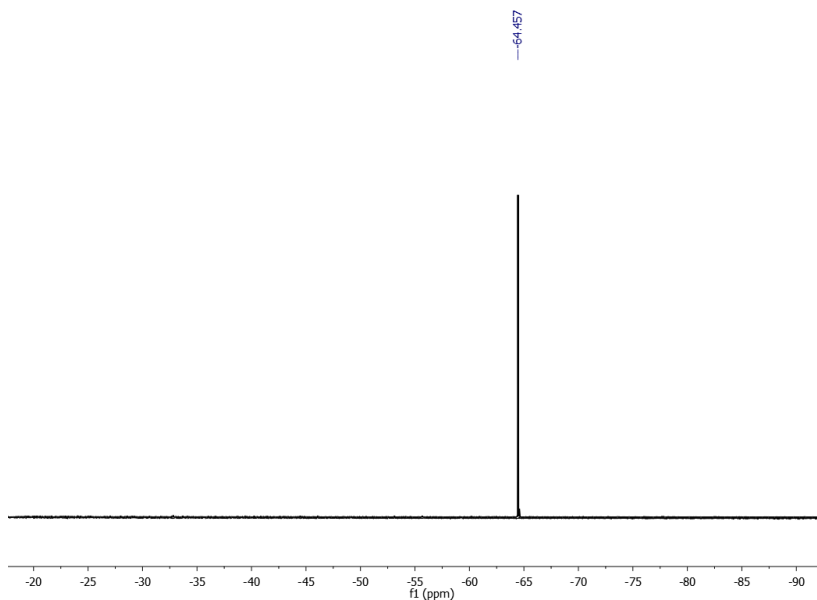


Figure S15. ^{19}F NMR spectrum (377 MHz) of complex **Pt2a** in CD_2Cl_2 .

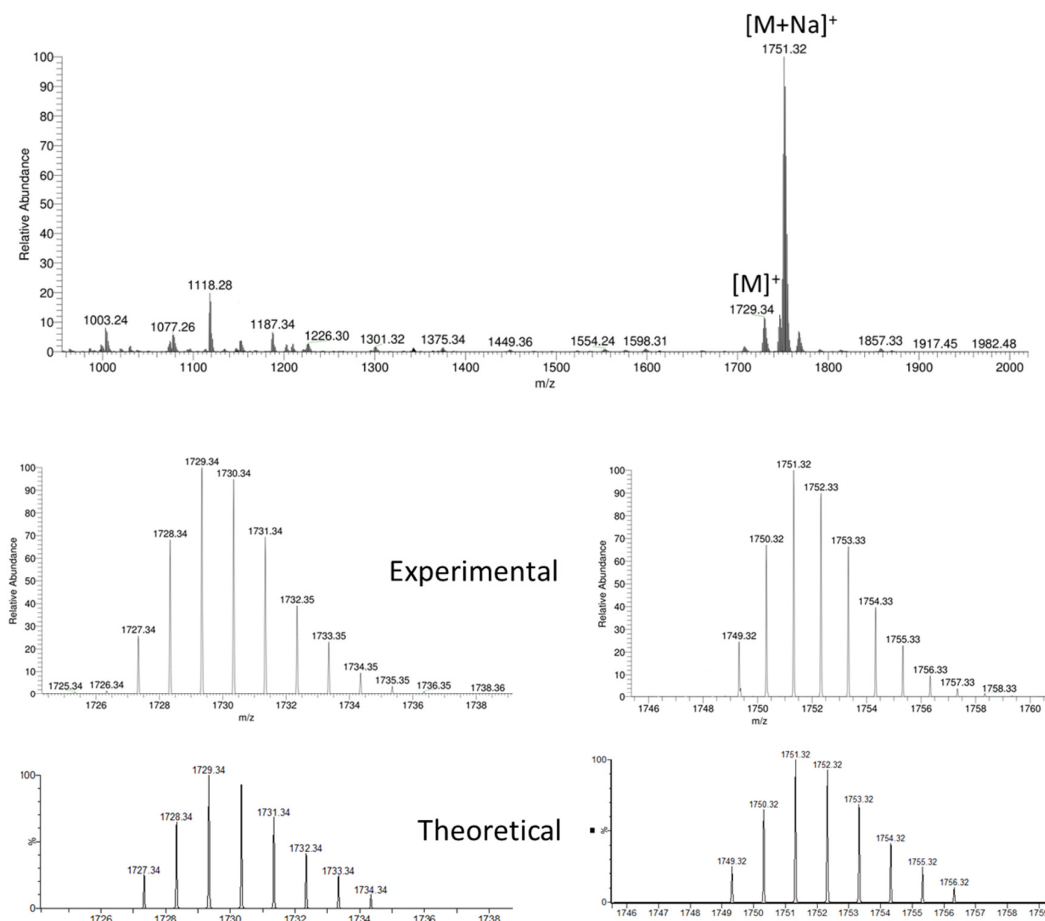


Figure S16. ESI-MS spectrum of complex **Pt2a** and isotopic distribution of peaks.

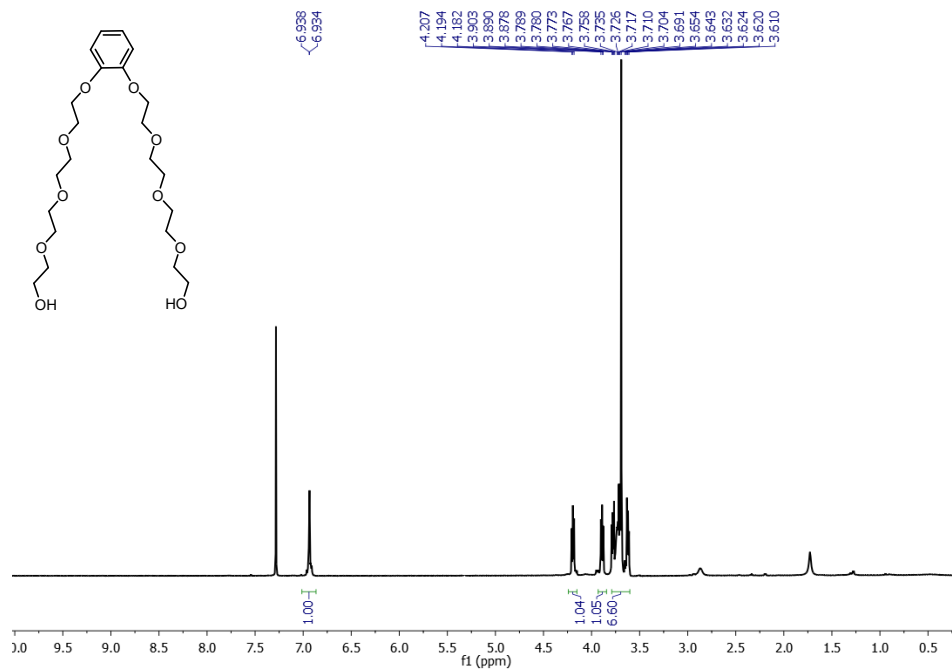


Figure S17. ¹H NMR spectrum of **3** in CDCl₃ (400 MHz).

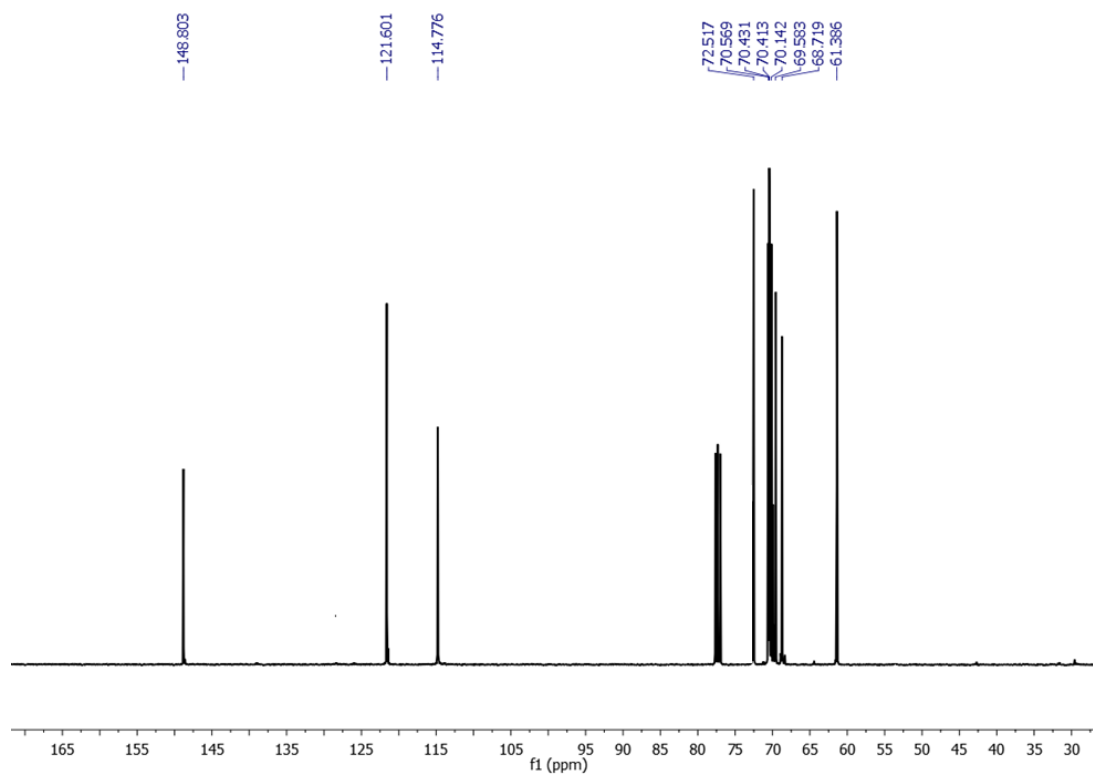


Figure S18. ¹³C NMR spectrum of **3** in CDCl₃ (100 MHz).

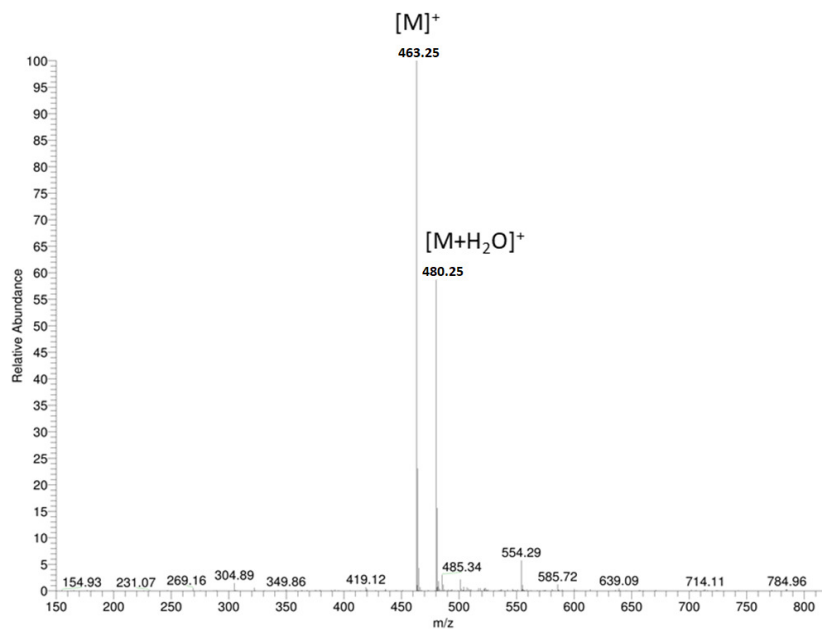


Figure S19. ESI-MS spectrum of **3**.

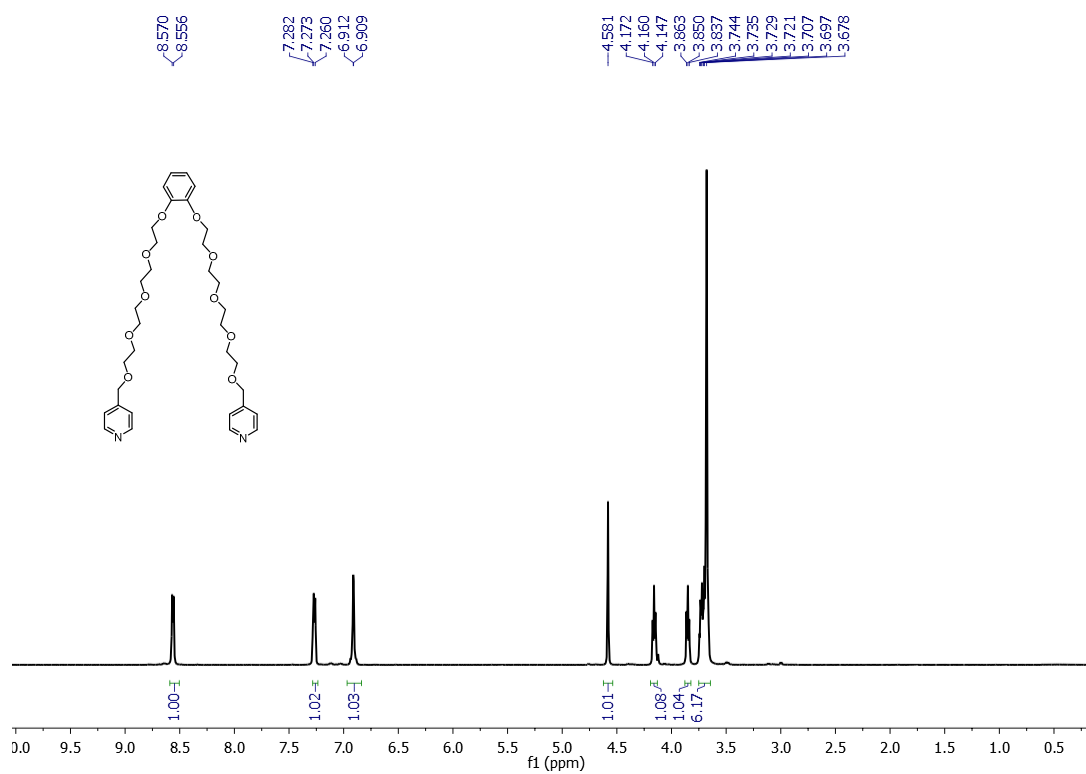


Figure S20. ^1H NMR spectrum of linker **L2b** in CDCl_3 (400 MHz).

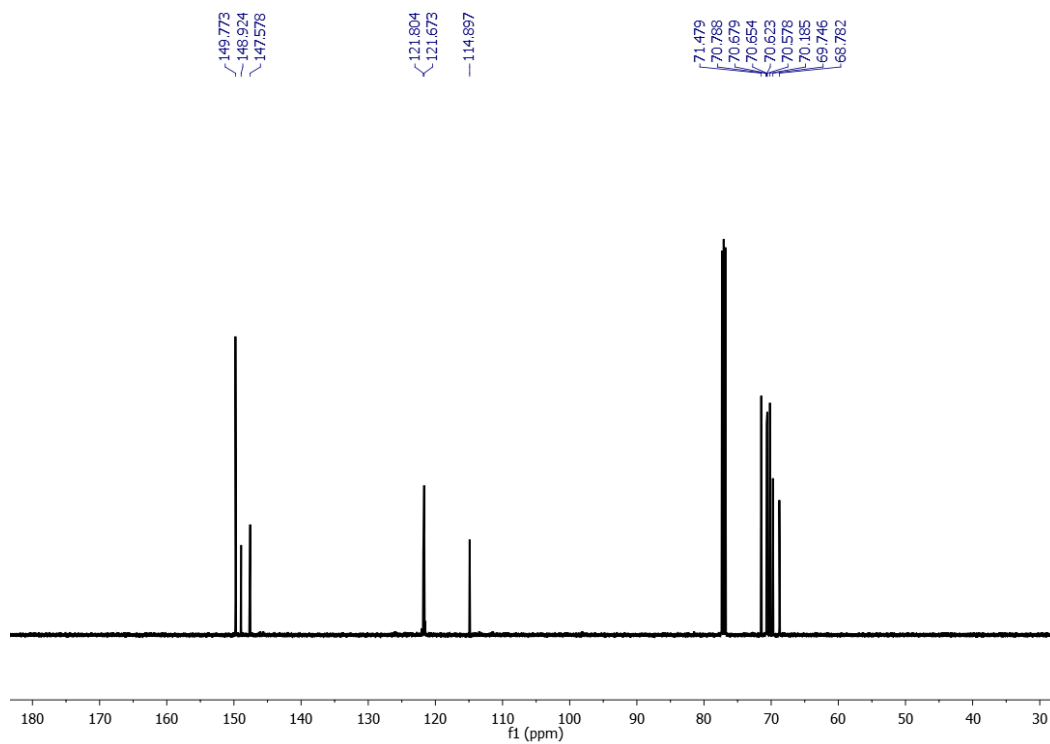


Figure S21. ¹³C NMR spectrum of linker **L2b** in CDCl₃ (100 MHz).

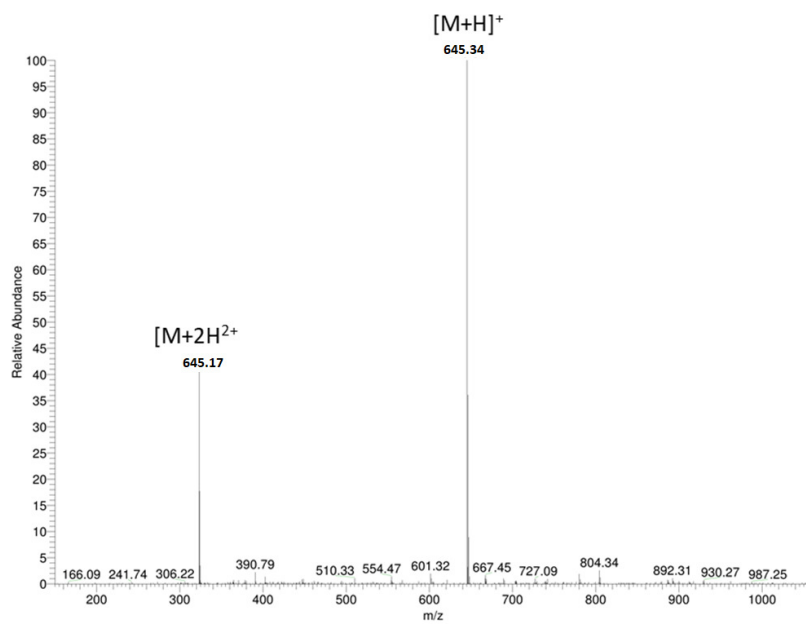


Figure S22. ESI-MS of linker **L2b**.

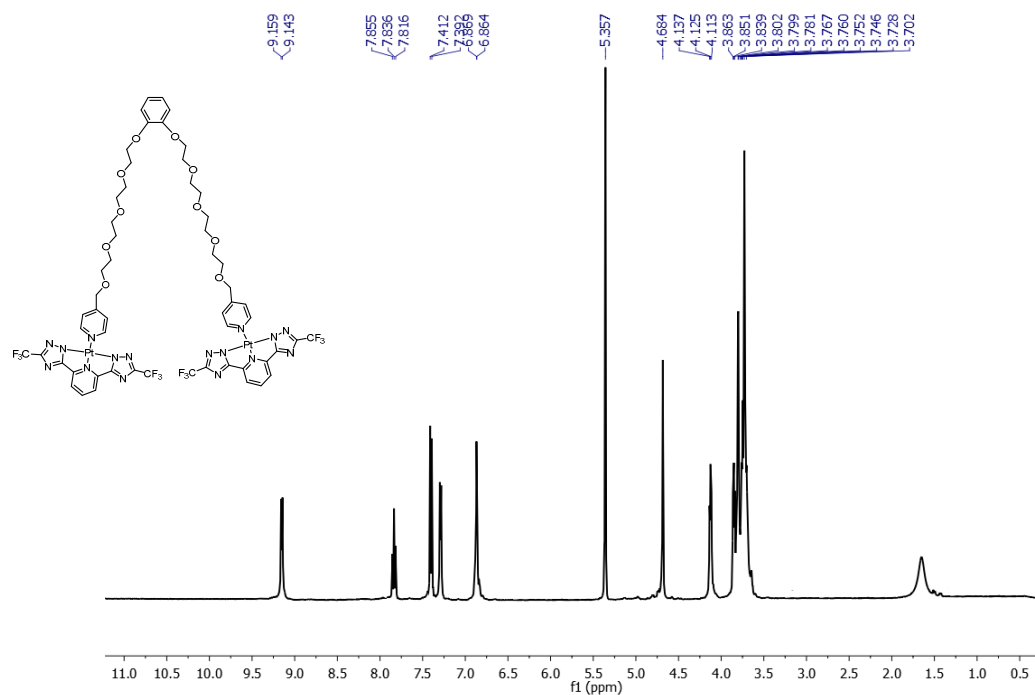


Figure S23. ^1H NMR spectrum of linker **Pt2b** in CD_2Cl_2 (400 MHz).

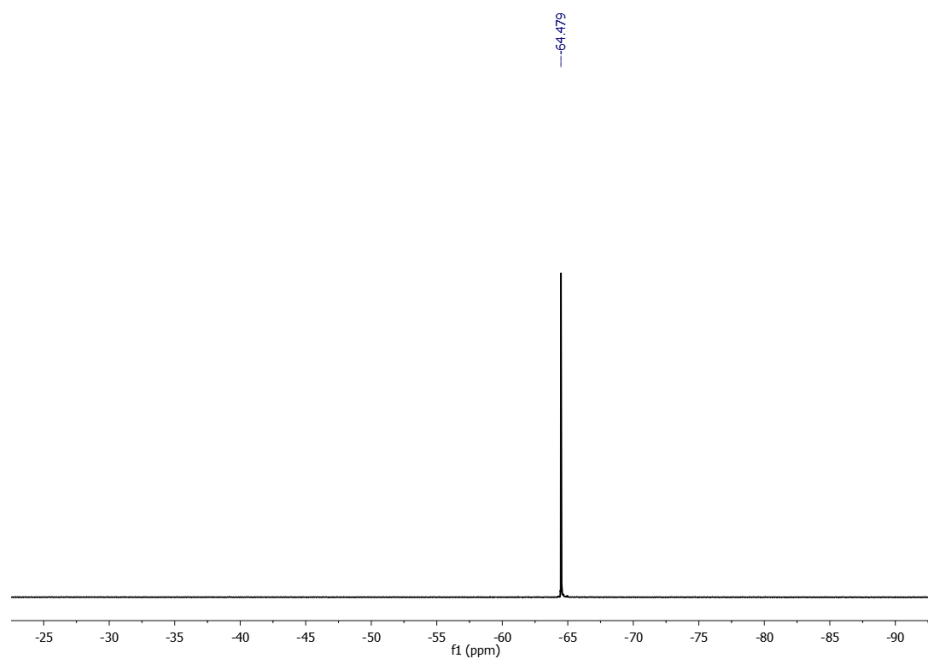


Figure S24. ^{19}F NMR spectrum of linker **Pt2b** in CD_2Cl_2 (377 MHz).

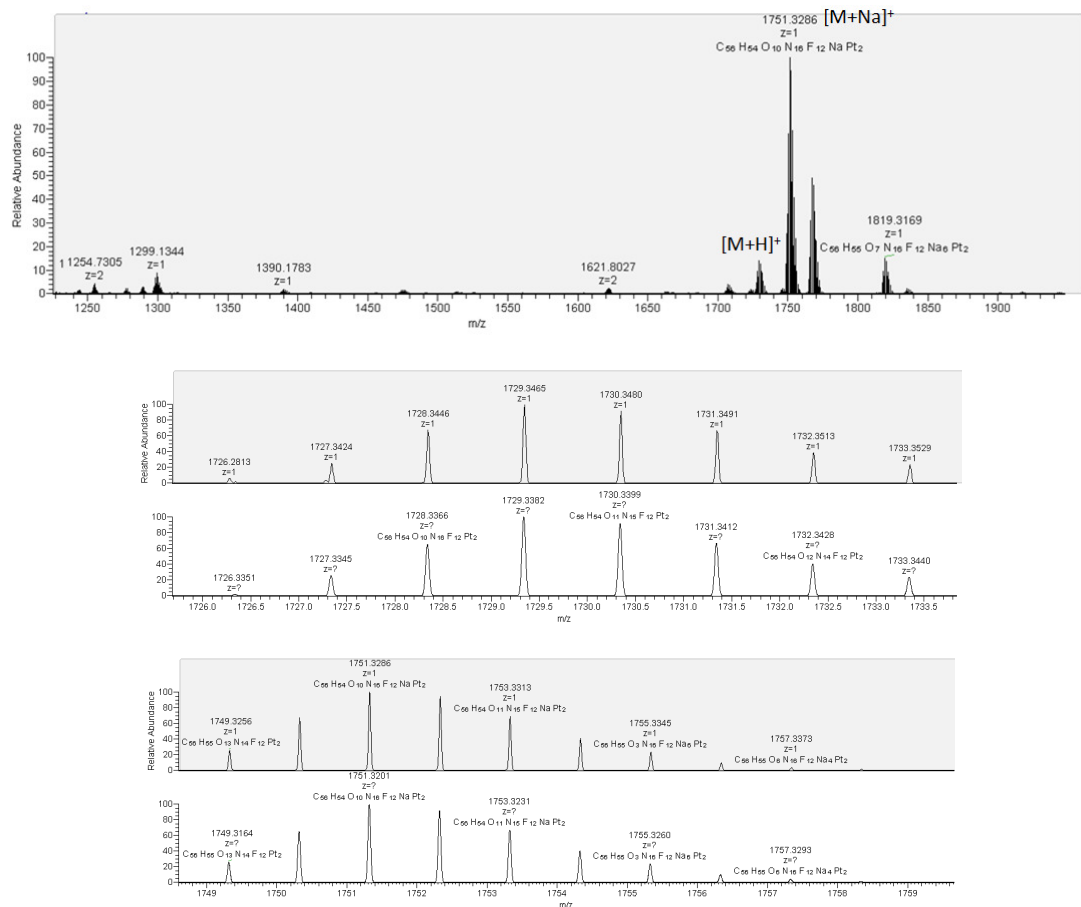


Figure S25. ESI-MS spectrum of complex **Pt2b** and isotopic distribution of peaks.

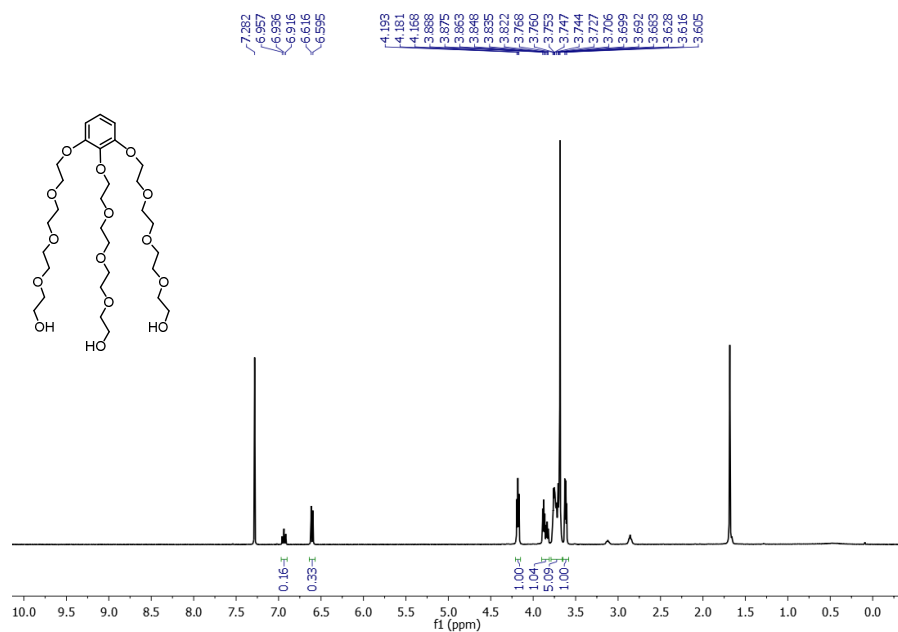


Figure S26. ^1H NMR spectrum of **4** in CDCl_3 (400 MHz).

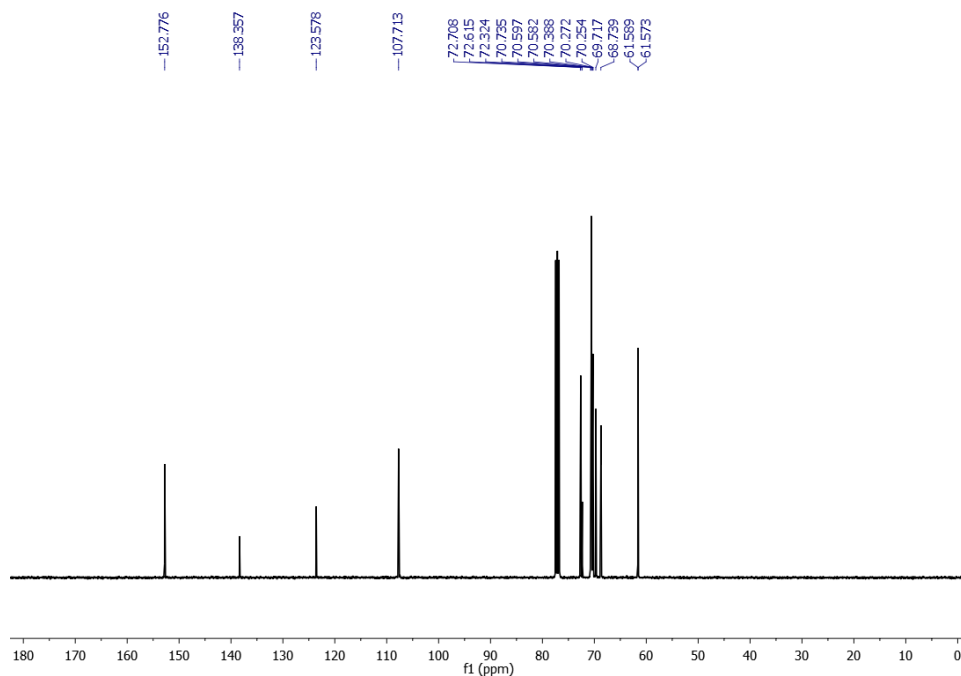


Figure S27. ^{13}C NMR spectrum of **4** in CDCl_3 (400 MHz).

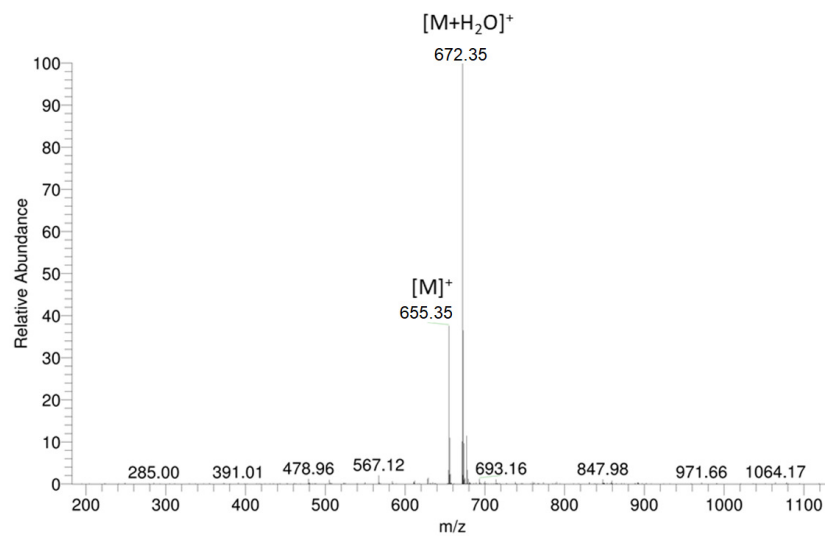


Figure S28. ESI-MS of compound **4**.

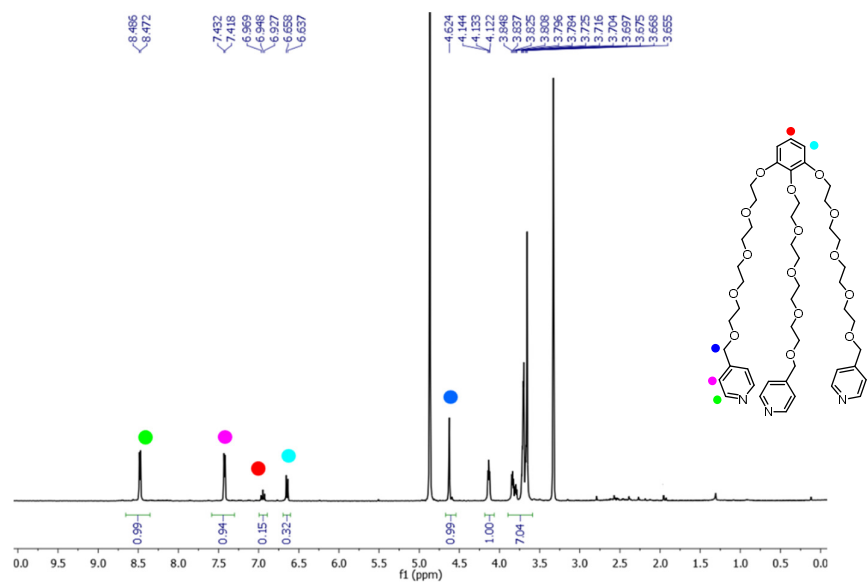


Figure S29. ¹H NMR spectrum of linker **L3** in CDCl₃ (400 MHz).

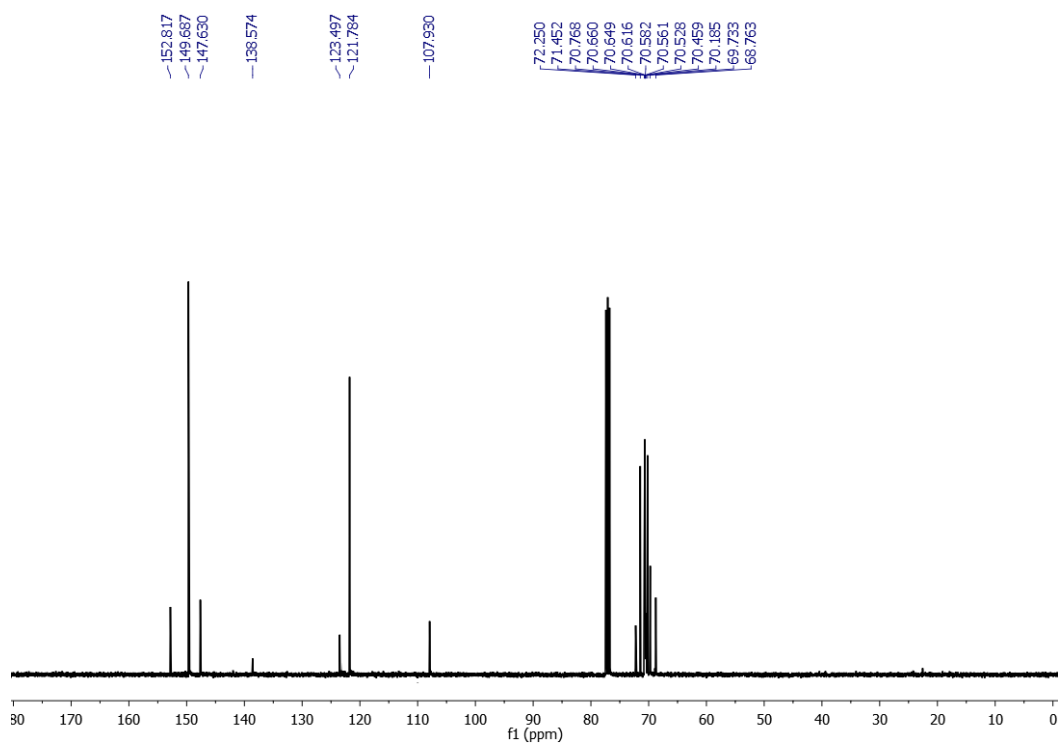


Figure S30. ¹³C NMR spectrum of linker **L3** in CDCl₃ (100 MHz).

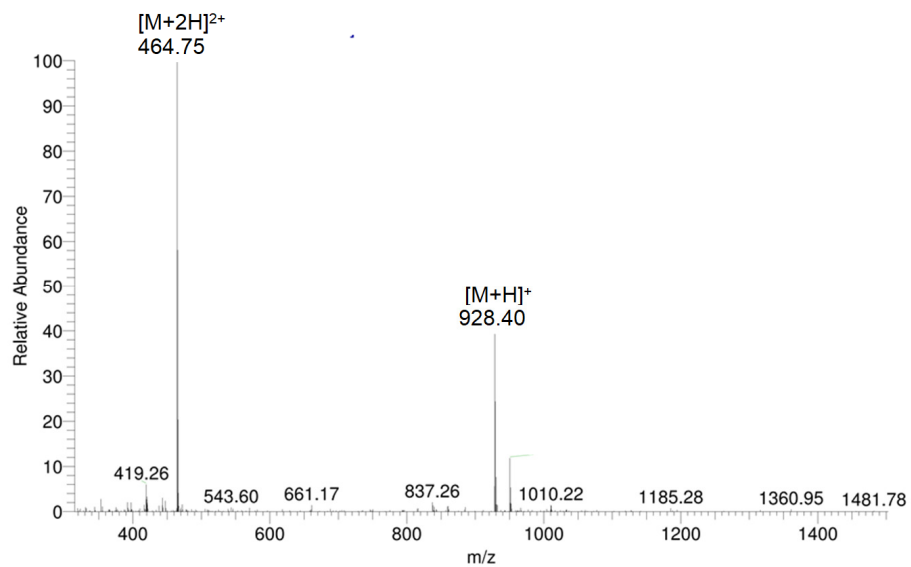


Figure S31. ESI-MS of Linker **L3**.

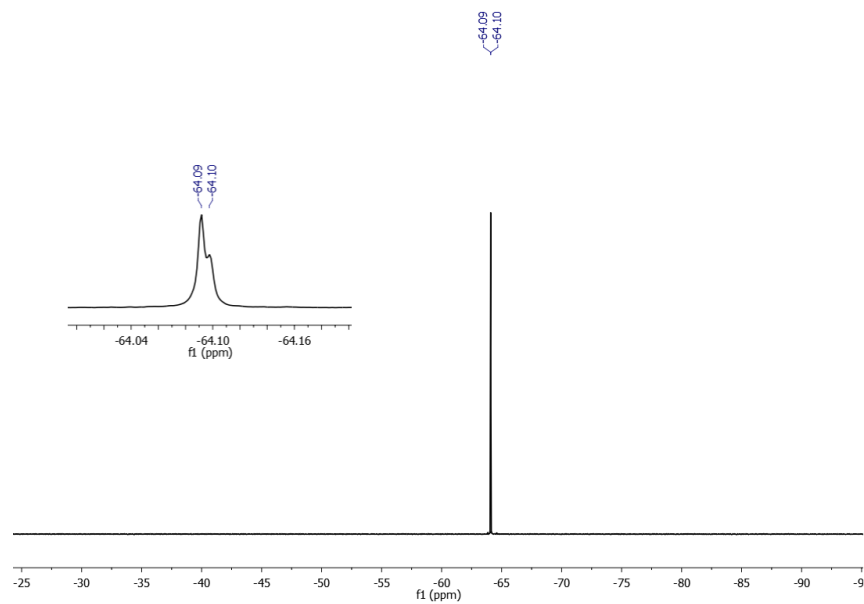


Figure S32. ^{19}F NMR spectrum of linker Complex **Pt3** in CD_2Cl_2 (377 MHz).

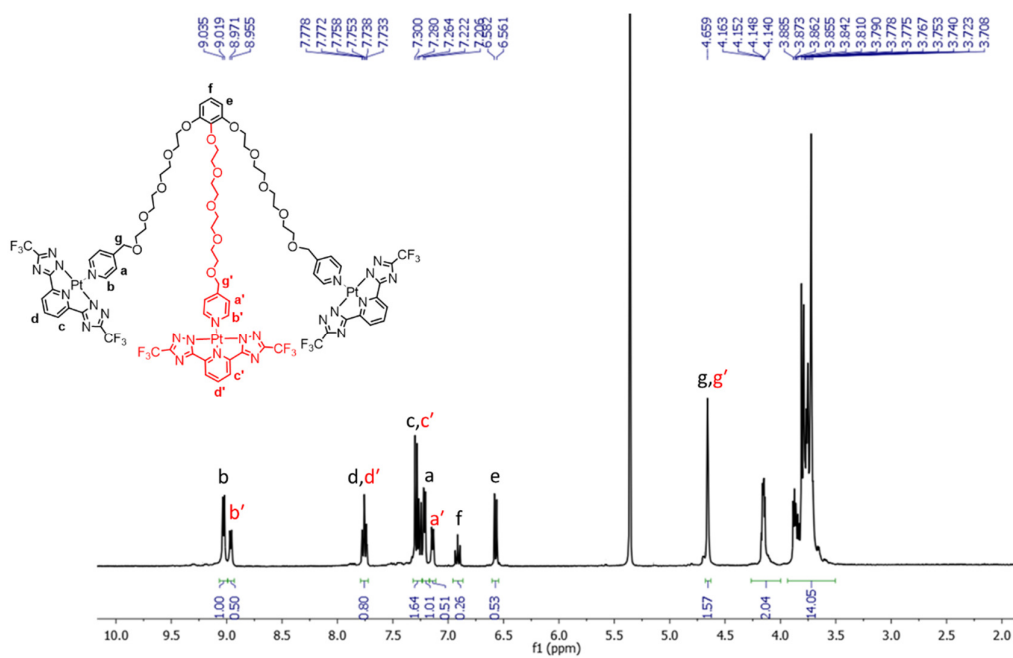


Figure S33. ^1H NMR spectrum of linker Complex **Pt3** in CD_2Cl_2 (400 MHz).

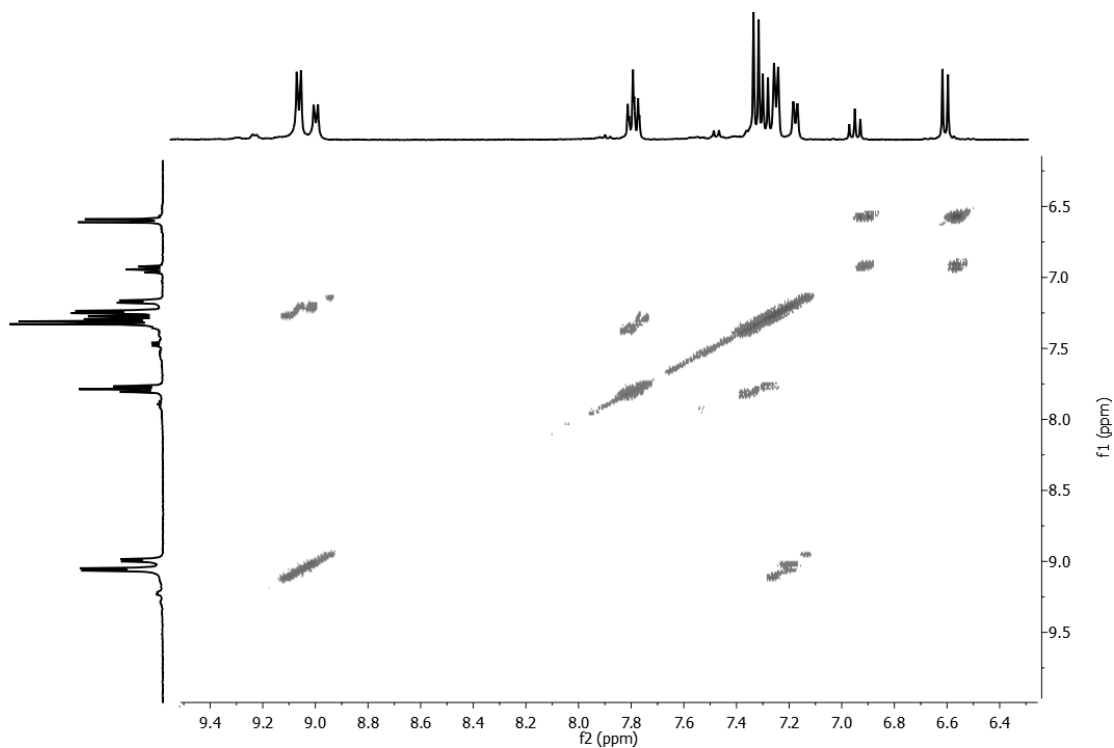


Figure S34. ^1H - ^1H COSY NMR spectrum of linker Complex **Pt3** in CD_2Cl_2 (400 MHz).

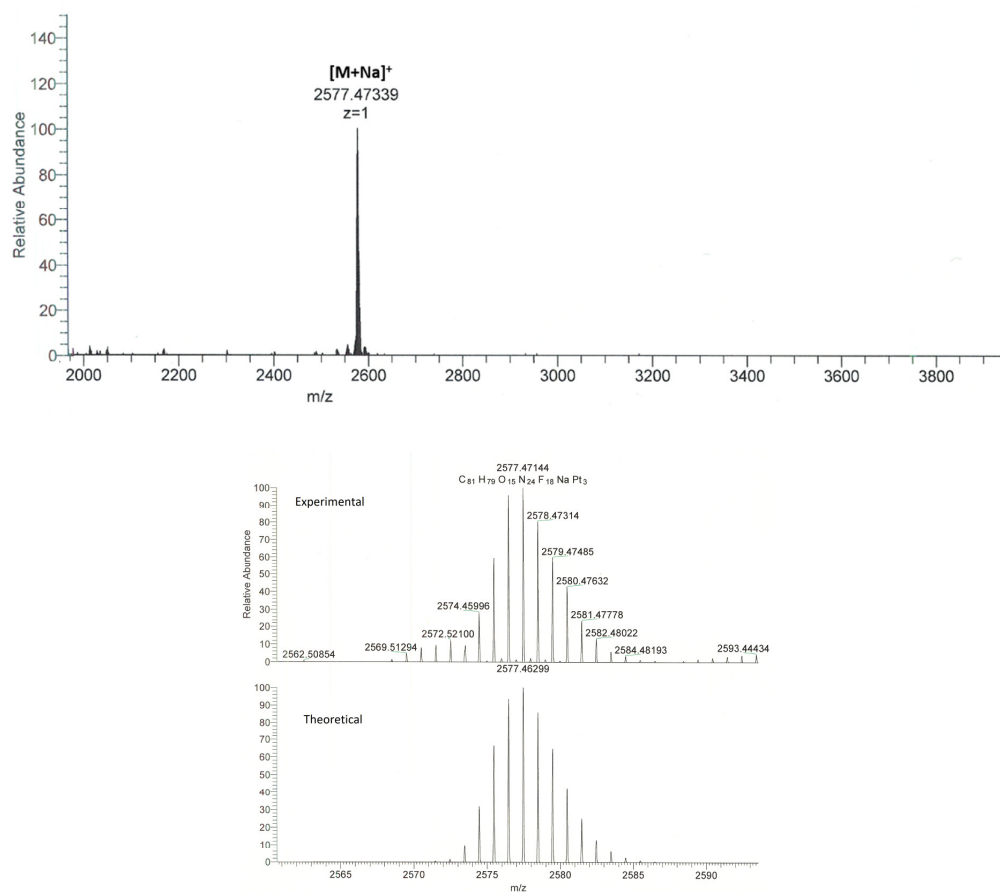


Figure S35. ESI-MS spectrum of complex **Pt3** and isotopic distribution of peak.

Photophysical data of Platinum Complexes.

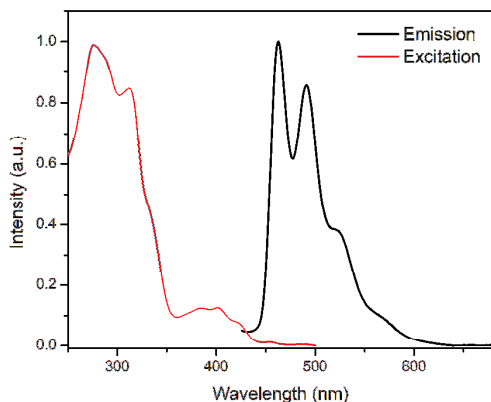


Figure S36. Normalized excitation and emission spectra of **Pt1** in DCM (5×10^{-5} M). Excitation and emission spectra were collected at the $\lambda_{em} = 535$ nm and upon λ_{exc} at 375 nm, respectively.

Table S1. Excited state lifetimes for complex **Pt1** in DCM at different concentration in the range 0.1 mM to 1.0 μ M recorded at $\lambda_{em} = 460$ nm, upon $\lambda_{exc} = 375$ nm.

Concentration (M)	Lifetime, τ , ns	
1×10^{-4}	$\tau_1 = 178$ (87%)	$\tau_2 = 3.8$ (13%)
5×10^{-5}	$\tau_1 = 188$ (88%)	$\tau_2 = 3.8$ (12%)
1×10^{-5}	$\tau_1 = 177$ (85%)	$\tau_2 = 3.7$ (15%)
5×10^{-6}	$\tau_1 = 177$ (82%)	$\tau_2 = 3.5$ (18%)
1×10^{-6}	$\tau_1 = 166$ (62%)	$\tau_2 = 3.1$ (38%)

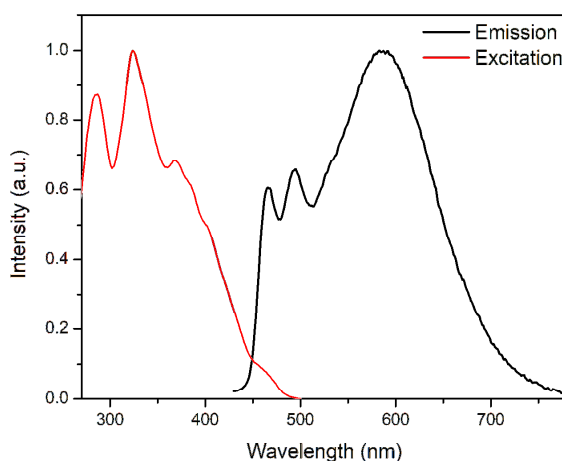


Figure S37. Normalized excitation and emission spectra of **Pt2a** in DCM (5×10^{-5} M). Excitation and emission spectra were collected at the $\lambda_{em} = 580$ nm and upon λ_{exc} at 375 nm, respectively.

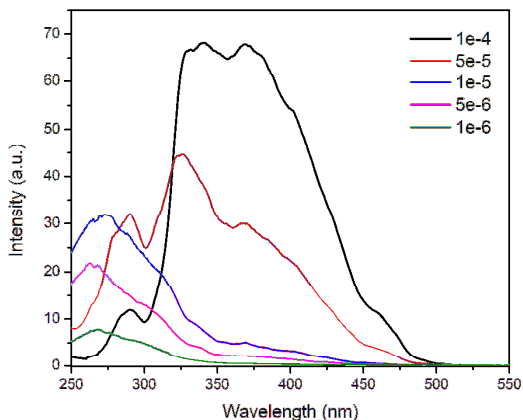


Figure S38. Left: Excitation spectra of **Pt2a** at variable concentration (0.1 mM to 1.0 μ M) in DCM collected at the $\lambda_{em} = 580$ nm.

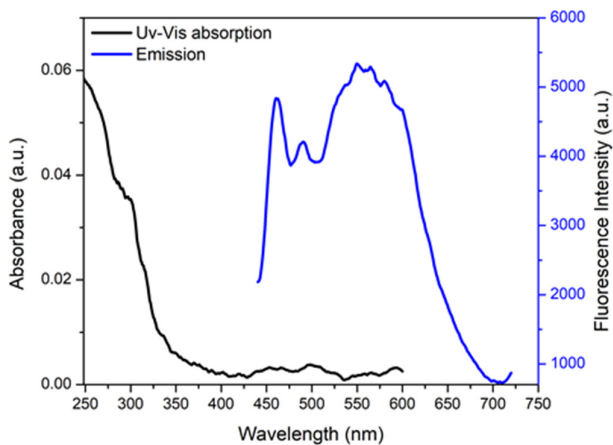


Figure S39. Uv-Vis and Emission spectra of deaerated DCM (1.0 μ M) solution of **Pt2a**.

Table S2. Excited state lifetime data for complex **Pt2a** in DCM at different concentration in the range 0.1 mM to 1.0 μ M recorded at $\lambda_{em} = 460$ nm and 580 nm, upon $\lambda_{exc} = 375$ nm.

Concentration (M)	580 nm		460 nm	
	Lifetime, τ , ns		Lifetime, τ , ns	
1×10^{-4}	$\tau_1 = 1050$ (94%)	$\tau_2 = 15.4$ (6%)	$\tau_1 = 282$ (91%)	$\tau_2 = 14.5$ (10%)
5×10^{-5}	$\tau_1 = 1010$ (88%)	$\tau_2 = 14.6$ (12%)	$\tau_1 = 258$ (88%)	$\tau_2 = 12.0$ (12%)
1×10^{-5}	$\tau_1 = 851$ (75%)	$\tau_2 = 13.5$ (25%)	$\tau_1 = 214$ (84%)	$\tau_2 = 6.0$ (16%)
5×10^{-6}	$\tau_1 = 782$ (71%)	$\tau_2 = 13.2$ (28%)	$\tau_1 = 191$ (79%)	$\tau_2 = 4.0$ (21%)
1×10^{-6}	$\tau_1 = 702$ (62%)	$\tau_2 = 12.8$ (38%)	$\tau_1 = 212$ (78%)	$\tau_2 = 11.5$ (17%)
Deaerated	$\tau_1 = 1100$ (66%)	$\tau_2 = 12.6$ (34%)	$\tau_1 = 273$ (68%)	$\tau_2 = 12.0$ (21%)

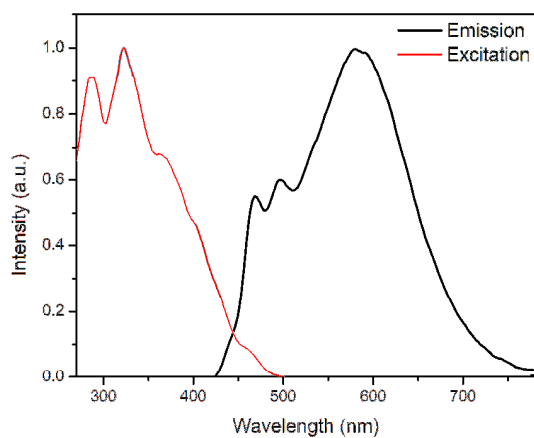


Figure S40. Normalized excitation and emission spectra of **Pt2b** in DCM (5×10^{-5} M). Excitation and emission spectra were collected at the $\lambda_{em} = 580$ nm and upon λ_{exc} at 375 nm, respectively.

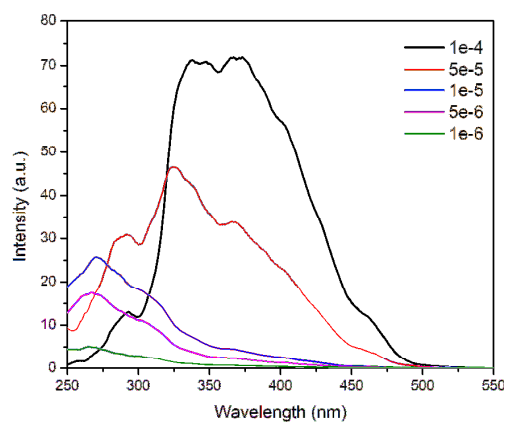


Figure S41. Left: Excitation spectra of **Pt2b** at variable concentration (0.1 mM to 1.0 μ M) in DCM collected at the $\lambda_{em} = 580$ nm.

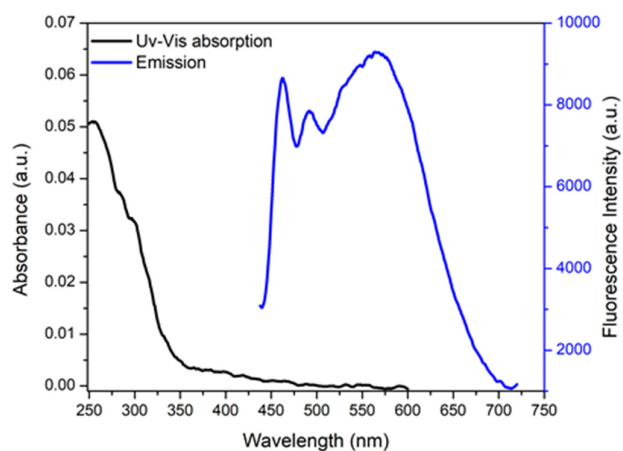


Figure S42. Uv-Vis and Emission spectra of deaerated DCM (1.0 μ M) solution of **Pt2b**.

Table S3. Excited state lifetimes for complex **Pt2b** in DCM at different concentration in the range 0.1 mM to 1.0 μ M recorded at $\lambda_{em} = 460$ nm and at 580 nm, upon $\lambda_{exc} = 375$ nm.

Concentration (M)	580 nm	460 nm
	Lifetime, τ , ns	Lifetime, τ , ns
1×10^{-4}	$\tau_1 = 1070$ (76%) $\tau_2 = 23$ (24%)	$\tau_1 = 251$ (41%) $\tau_2 = 14.8$ (59%)
5×10^{-5}	$\tau_1 = 1030$ (66%) $\tau_2 = 22$ (34%)	$\tau_1 = 236$ (38%) $\tau_2 = 14.5$ (62%)
1×10^{-5}	$\tau_1 = 855$ (52%) $\tau_2 = 24$ (48%)	$\tau_1 = 228$ (26%) $\tau_2 = 15.6$ (74%)
5×10^{-6}	$\tau_1 = 796$ (33%) $\tau_2 = 20$ (67%)	$\tau_1 = 193$ (40%) $\tau_2 = 12.0$ (60%)
1×10^{-6}	$\tau_1 = 708$ (44%) $\tau_2 = 22$ (56%)	$\tau_1 = 207$ (64%) $\tau_2 = 18.2$ (27%)
1×10^{-6} Deaerated	$\tau_1 = 902$ (53%) $\tau_2 = 24$ (47%)	$\tau_1 = 247$ (60%) $\tau_2 = 18.5$ (28%)

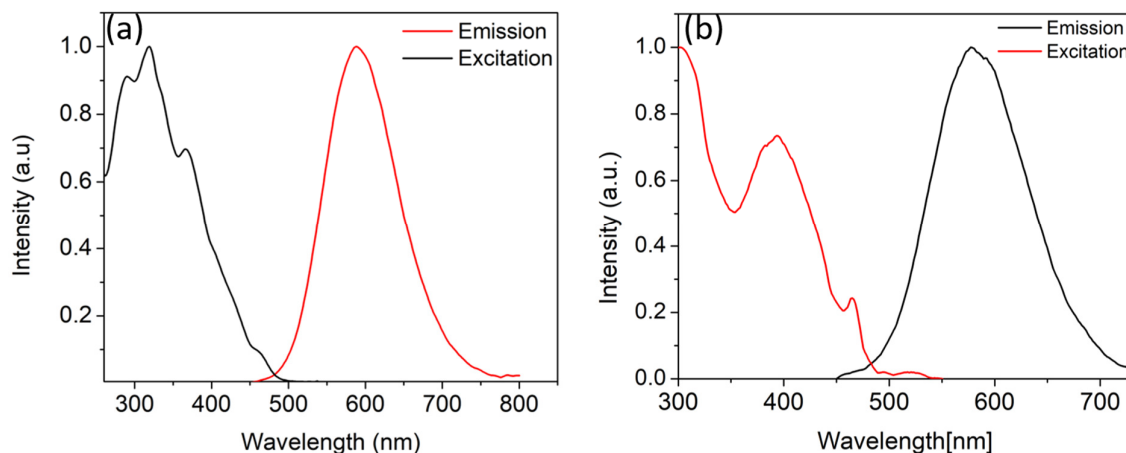


Figure S43. (a) Normalized excitation and emission spectra of **Pt3** in DCM (5×10^{-5} M). (b) Normalized excitation and emission spectra of deaerated DCM solution of **Pt3** (1×10^{-6} M). Excitation and emission spectra were collected at the $\lambda_{em} = 600$ nm and upon λ_{exc} at 400 nm, respectively.

Table S4. Excited state lifetimes for complex **Pt3** in DCM at different concentration in the range 0.1 mM to 1.0 μ M recorded at $\lambda_{em} = 580$ nm, upon $\lambda_{exc} = 375$ nm.

Concentration (M)	Lifetime, τ , μ s
1×10^{-4}	1.08
5×10^{-5}	1.09
1×10^{-5}	1.12
5×10^{-6}	1.12
1×10^{-6}	1.22

References

1. S. Sinn, F. Biedermann and L. De Cola, *Chemistry - A European Journal*, 2017, **23**, 1965-1971.